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ABSTRACT

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Proftest SYKE carried out the proficiency test in cooperation with KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste material in May-June 2020. The results of the two stage batch leaching test (EN 12457-3) for samples of treated slag from waste combustion were compared and evaluated. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, F^-, SO_4^{2-}, DOC, pH, conductivity, and TDS. In total, 13 participants joined in the proficiency test.

In this proficiency test either the robust mean or the median of the results reported by the participants was used as the assigned value. The results were evaluated both with z and E_n scores. When deviation of 10–35 % or 0.3-0.4 pH units was accepted from the assigned value, 85 % of the results evaluated with z scores were satisfactory. Of the results evaluated with E_n scores, 80 % were satisfactory.

Warm thanks to all the participants of this proficiency test!

Keywords: leaching test, two stage batch leaching test, waste landfill acceptance criteria, environmental laboratories, proficiency test, interlaboratory comparisons

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 04/2020

Proftest SYKE järjesti yhteistyössä KVVY Tutkimus Oy:n kanssa pätevyyskokeen touko-kesäkuussa 2020 laboratorioille, jotka tekevät liukoisuustestejä jätteiden kaatopaikkakelpoisuuden arvioimiseksi (LT 04/2020). Pätevyyskokeessa vertailtiin kaatopaikkakelpoisuuden selvittämisessä käytettävän 2-vaiheisen ravistelutestin (SFS-EN 12457-3) määritystuloksia jätteenpolton seulotuista pohjakuona-näytteistä. Määritettävät testisuureet olivat metallit (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, F^-, SO_4^{2-}, DOC, pH, sähkönjohtavuus ja TDS. Pätevyyskokeessa oli yhteensä 13 osallistujaa.

Testisuureiden vertailuarvona käytettiin osallistujatulosten robustia keskiarvoa tai niiden mediaania. Tuloksia arvioitiin sekä z- että E_n-arvoilla. Kun tulosten sallittiin vaihdella 10–35 % tai 0,3–0,4 pH yksikköä vertailuarvosta, 85 % z-arvoilla arvioiduista tuloksista oli hyväksyttäviä. E_n-arvoilla arvioiduista tuloksista oli hyväksyttyjä 80 %.

Kiitos pätevyyskokeen osallistujille!

Avainsanat: liukoisuustesti, kaksivaiheinen ravistelutesti, kaatopaikkakelpoisuus, ympäristö-laboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 04/2020

Proftest SYKE genomförde i samarbete med föreningen KVVY Tutkimus Oy en provningsjämförelse under maj-juni 2020 för laktester som används vid bedömningen av avfall som ska deponeras på deponi. Tillsammans 13 laboratorier deltog i jämförelse.

Som referensvärde av analytens koncentration användes det robust medelvärdet eller median av deltagarnas resultat. I jämförelsen 85 % av resultaten som värderas med hjälp z värdet var acceptabla, när totalavvikelsen 10–35 % eller 0,3–0,4 pH enhet från referensvärdet accepterades. Resultaten som värderades med hjälp E_n värdet var 78 % acceptabla.

Ett varmt tack till alla deltagarna i testet!

Nyckelord: laktest, tvåstegs skaktest, klassificering av avfall för deponi, miljölaboratorier, provningsjämförelse, kompetensprövning

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) in cooperation with KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste material in May-June 2020 (LT 04/2020). In this PT the results of the two stage batch leaching test (EN 12457-3 [1]) for samples of treated slag from waste combustion were compared and evaluated. The two stage batch leaching test is used as a compliance test in evaluation the waste landfill disposal. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, F^-, SO_4^{2-}, DOC, pH, conductivity, and TDS.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [2] and applying ISO 13528 [3] and IUPAC Technical report [4]. The Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
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Phone: +358 295 251 000, email: proftest@environment.fi

The responsibilities in organizing the proficiency test

Riitta Koivikko	coordinator
Mirja Leivuori	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance

Cooperation partner

KVVY Tutkimus Oy (KVVY, T064, www.finas.fi/sites/en)

Analytical experts

Two stage batch leaching test	Marika Kaasalainen (KVVY)
Metals	Timo Sara-Aho (SYKE)
pH and conductivity	Raija Ivalo (KVVY)
Anions (IC)	Suvi Pöyhönen (KVVY)
DOC	Tea Niemistö (KVVY)

Subcontracting KVVY: Sample material preparation, homogenization and dividing into subsamples, leaching test (pretest, homogeneity) and the needed chemical and physico-chemical analysis.

2.2 Participants

In total 13 laboratories participated in this proficiency test (Appendix 1), 10 from Finland and 3 from abroad. Altogether 62 % of the participants used accredited analytical methods at least for a part of the measurements. For this proficiency test, the expert laboratory has the code 4 (KVVY Tutkimus Oy, T064, http://www.finas.fi/sites/en) in the results tables.

2.3 Samples and delivery

The sample RT1 delivered to the participants was treated slag from waste combustion collected from Finland (sample size about 250 g). This waste is included in the scopes of the Government Decree 591/2006 and the Government Decree 843/2017 [5, 6]. The sample material was homogenized prior to dividing into sub samples. Particle size was < 4 mm according to the leaching test standard (EN 12457-3) [1].

The used sample codes in the result tables were:

RT1LS_2 Sample RT1, two stage batch leaching test, L/S 2
RT1LS_8 Sample RT1, two stage batch leaching test, L/S 8
RT1LS10 Sample RT1, two stage batch leaching test, L/S 10

The samples were delivered on 21 April 2020 to the participants abroad and on 22 April 2020 to the national participants. The samples arrived to the participants at the latest on 24 April 2020.

The two stage batch leaching test was requested to be conducted at the latest on 3 June 2020.

Determinations from the leaching test eluates were:

- L/S 2 and L/S 10:
  - metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn)
  - Cl^-, F^-, SO_4^{2-}
  - DOC, TDS
- L/S 2 and L/S 8:
  - conductivity, pH

The results were requested to be reported latest on 16 June 2020. The participants delivered the results mainly accordingly, but two participants delivered the results on 17 June 2020.

The preliminary result report was delivered to the participants via ProftestWEB and email on 26 June 2020.

2.4 Sample pretesting and homogeneity

The material suitability for two stage batch leaching test was tested by conducting the two stage batch leaching test and analyzing all the measurands prior dividing the material into subsamples.

The homogeneity of the samples was tested by conducting one stage batch leaching test for 4 samples and by analyzing the measurands: Ba, Cr, Cu, Mo, Sb, Zn, V, Cl^-, F^-, DOC, pH, and conductivity (Appendix 2). According to the homogeneity test results, the samples were considered homogenous.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 3. The comments from the participants dealt with the results form and erroneously reported results. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Hampel or the Grubbs test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result was reported as below detection limit, it was not included in the statistical calculations.

More information about the statistical handling of the data is available from the Guide for participant [7].

2.6.2 Assigned values

The detailed information of the assigned values, their uncertainties and reliability are shown in Appendix 4.

The leachability for As, Cd, F, Hg, Ni, Pb, and Zn was very low and for many participants close or below the limit of detection/quantification. Thus, the assigned value was not set for following measurands in the eluates:

- RT1LS_2: As, Cd, F, Hg, Ni, Pb, Zn
- RT1LS10: Cd, Hg, Pb, Zn

The robust mean of the results reported by the participants was used as the assigned value for SO_4 in RT1LS10. For all the other evaluated measurands the median of the results reported by

the participants was used as the assigned value (n_{stat} < 12, Appendix 4). The expanded uncertainty of the assigned value was calculated using the standard deviation of the reported results [3].

The used assigned values are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned values was statistically tested [3, 4].

The expanded uncertainty of the assigned values varied between 1.0 % and 12 % for the measurands evaluated with z scores and between 24 % and 76 % for the measurands evaluated with E_n scores (Appendix 4, Chapter 2.6.3).

In the preliminary result report, the assigned value and its uncertainty were given also to Ni in RT1LS_2. Due to high variation of the reported results, the assigned value is not given for Ni in RT1LS_2 in final results evaluation.

After reporting the preliminary results no other changes have been done for the assigned values.

2.6.3 Proficiency assessment procedure

The results of this proficiency test were evaluated both with z and E_n scores.

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity test, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2 \times s_{pt}$ at the 95 % confidence level) was set to 0.3–0.4 pH units and to 10–35 % for the other measurands, depending on the measurand and leaching step. When the number of reported results was low (n_{stat} < 6) or the deviation of the result was very high, the standard deviation was not set and the proficiency estimation as z scores is not given.

After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.

In this proficiency test, the performance evaluation was done by means of E_n scores ('*Error, normalized*', [3]) for those measurands where the number of reported results was low (n_{stat}<6) or the deviation of the results was very high, but the assigned value and its uncertainty were set:

- RT1LS_2: Ba, Se
- RT1LS10: As, F, Ni, Se

In the preliminary result report, the assigned value and its uncertainty were given also to Ni in RT1LS_2 and the performance evaluation was done by means of E_n scores. Due to high variation of the reported results, the performance evaluation is not given for Ni in RT1LS_2 in final results evaluation.

E_n scores are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

Scores of E_n $-1.0 < E_n < 1.0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1.0$ or $E_n \leq -1.0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

When using the robust mean or the median of the reported results as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value and s_{pt} is the standard deviation for proficiency assessment [3, 4]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the standard deviation for proficiency assessment and the corresponding z score was estimated by comparing the standard deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standards deviation (s, $n_{stat}<12$) of the reported results [3, 4]. The criterion s_{rob} or $s / s_{pt} < 1.2$ was mainly fulfilled.

In the following case, the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurand
RT1LS_2	Sb

3 Results and conclusions

3.1 Results

The summary of the results of the proficiency test is presented in Table 1. The terms in the results table are explained in Appendix 5. The results and the performance of each participant are presented in Appendix 6 and reported results with their expanded uncertainties (k=2) are presented in Appendix 7. The summaries of the z and E_n scores are shown in Appendices 8 and 9, and the z scores in the ascending order in Appendix 10.

Table 1. The summary of the results in the proficiency test LT 04/2020.

Measurand	Sample	Unit	Assigned value	Mean	Median	s	s %	Rob. mean	s_{rob}	s_{rob} %	2 x s_{pt} %	n_{all}	Acc z %	Acc. E_n %
As	RT1LS_2	mg/kg	-	0.013	0.006	0.018	134.2	-	-	-	-	11	-	-
	RT1LS10	mg/kg	0.024	0.025	0.024	0.014	55.7	-	-	-	-	12	-	100
Ba	RT1LS_2	mg/kg	0.096	0.110	0.096	0.037	33.9	0.120	0.052	43.0	-	11	-	71
	RT1LS10	mg/kg	0.42	0.41	0.42	0.05	11.8	0.45	0.11	24.3	25	12	80	-
Cd	RT1LS_2	mg/kg	-	0.036	0.036	0.000	0.0	-	-	-	-	11	-	-
	RT1LS10	mg/kg	-	0.020	0.020	0.024	120.2	-	-	-	-	12	-	-
Cl	RT1LS_2	mg/kg	4726	4753	4726	253	5.3	4753	287	6.0	15	11	91	-
	RT1LS10	mg/kg	4975	4995	4975	173	3.5	5020	206	4.1	10	12	83	-
Conductivity 25	RT1LS_2	mS/m	1185	1172	1185	79	6.7	1177	77	6.5	15	10	90	-
	RT1LS_8	mS/m	198	197	198	9	4.5	200	12	6.1	15	10	80	-
Cr	RT1LS_2	mg/kg	2.09	2.07	2.09	0.15	7.4	2.10	0.20	9.6	25	12	83	-
	RT1LS10	mg/kg	2.71	2.82	2.71	0.26	9.1	2.81	0.27	9.6	25	13	92	-
Cu	RT1LS_2	mg/kg	0.47	0.48	0.47	0.07	13.8	0.48	0.07	14.9	30	12	90	-
	RT1LS10	mg/kg	0.74	0.74	0.74	0.09	11.7	0.74	0.09	12.4	25	13	92	-
DOC	RT1LS_2	mg/kg	114	116	114	12	10.2	116	13	11.6	25	8	88	-
	RT1LS10	mg/kg	146	151	146	15	10.1	151	17	11.4	25	9	89	-
F	RT1LS_2	mg/kg	-	1.07	0.73	1.00	93.7	-	-	-	-	10	-	-
	RT1LS10	mg/kg	5.34	6.48	5.34	4.62	71.2	-	-	-	-	11	-	50
Hg	RT1LS_2	mg/kg	-	0.012	0.001	0.020	168.0	-	-	-	-	11	-	-
	RT1LS10	mg/kg	-	0.022	0.022	0.018	83.6	-	-	-	-	12	-	-
Mo	RT1LS_2	mg/kg	1.09	1.12	1.09	0.14	12.4	1.11	0.15	13.2	30	12	92	-
	RT1LS10	mg/kg	1.49	1.49	1.49	0.13	8.5	1.49	0.14	9.6	25	13	92	-
Ni	RT1LS_2	mg/kg	-	0.032	0.022	0.036	111.2	-	-	-	-	12	-	-
	RT1LS10	mg/kg	0.030	0.031	0.030	0.024	76.0	-	-	-	-	13	-	67
Pb	RT1LS_2	mg/kg	-	0.035	0.035	0.000	0.0	-	-	-	-	11	-	-
	RT1LS10	mg/kg	-	0.037	0.037	0.000	0.0	-	-	-	-	12	-	-
pH	RT1LS_2		9.78	9.77	9.78	0.16	1.7	9.77	0.18	1.9	4	12	67	-
	RT1LS_8		10.7	10.6	10.7	0.2	1.5	10.6	0.3	2.6	3	12	75	-
Sb	RT1LS_2	mg/kg	0.069	0.071	0.069	0.014	19.4	0.071	0.016	22.0	35	11	91	-
	RT1LS10	mg/kg	0.39	0.39	0.39	0.06	14.5	0.38	0.07	17.7	30	12	75	-
Se	RT1LS_2	mg/kg	0.022	0.027	0.022	0.015	53.6	-	-	-	-	11	-	100
	RT1LS10	mg/kg	0.052	0.051	0.052	0.023	45.7	-	-	-	-	12	-	100
SO_4	RT1LS_2	mg/kg	6150	6119	6150	219	3.6	5982	411	6.9	20	12	83	-
	RT1LS10	mg/kg	10053	9984	10105	1162	11.6	10053	1153	11.5	25	13	85	-
TDS	RT1LS_2	mg/kg	16594	16621	16594	1165	7.0	-	-	-	20	8	75	-
	RT1LS10	mg/kg	23228	23511	23228	1203	5.1	23511	1364	5.8	15	9	78	-
V	RT1LS_2	mg/kg	0.034	0.034	0.034	0.003	8.6	0.035	0.005	13.1	25	11	86	-
	RT1LS10	mg/kg	0.17	0.17	0.17	0.01	8.3	0.17	0.02	9.1	25	12	100	-
Zn	RT1LS_2	mg/kg	-	0.028	0.028	0.017	61.3	-	-	-	-	11	-	-
	RT1LS10	mg/kg	-	0.12	0.12	0.08	65.6	-	-	-	-	12	-	-

s: the standard deviation, s %: the standard deviation as percent, Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, n_{all}: the number of the participants, Acc z %: the results (%), where $|z| \leq 2$, Acc. E_n %: the results (%), where $|E_n| < 1$.

3.2 Analytical methods

The standard method EN 12457-3 (two stage batch leaching test) [1] was used to determine the leaching properties of studied measurands from the samples of treated slag from waste combustion. Within the two stage batch leaching test, the liquid to solid phase ratio is 2 l/kg dry matter in the first step and 8 l/kg dry weight in the second step. The cumulative release at the cumulative L/S10 is calculated from L/S2 and L/S8 results. The concentrations of the measurands are expressed as the leached amounts (mg/kg dry weight) relative to the total mass of the sample.

The descriptions of the procedures the participants followed were collected via Webropol questionnaire. Nine participants (69 %) replied to the questionnaire (Appendix 11). The procedures performed by the participants follow mainly the requirements of the standard method. Nevertheless, some differences in procedures used by the participants were observed (Appendix 11). The performance of participants was not observed to be affected directly from these differences.

The participants were allowed to use different analytical methods for the measurements of the measurands' concentrations in the PT. The measurements of metals were mostly done by ICP-MS and some participants used ICP-OES. The standard EN 16192 summarizes the analytical test methods for the waste eluates [8]. The statistical comparison of the analytical methods was not possible for the data due to low number of results. The used analytical test methods are listed in Appendix 12 and the reported results of the participants grouped by methods with their expanded uncertainties (k=2) are presented in Appendix 13.

The leaching test is known to be sensitive for the temperature of the analysis as well as for the filtration and agitation steps. The laboratory conditions during the leaching test are shown to be critical especially for Zn and Cu. During filtration, the device might retain or dissolve compounds, which might distort the results. Especially analysis of Pb has been shown to be affected by the filtration device. Therefore, careful validation procedures for the filtration devices should be used and, further, different filter materials and types should be thoroughly tested before operational use.

3.3 Uncertainties of the results

Altogether 77 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 2, Appendices 7 and 14). The range of the reported uncertainties varied between the measurands.

Several approaches were used for estimating the measurement uncertainty (Appendix 14). The mostly used approach was based on the data from method validation (Appendix 14). One participant used MUkit measurement uncertainty software for the estimation of their uncertainties [9]. The free software is available on the webpage: www.syke.fi/envical/en [9, 10]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Within the optimal measuring range, the expanded measurement uncertainty (k=2) should typically be 20–40%. Close to the limit of quantification the relative measurement uncertainty is higher. The harmonization of the uncertainties estimation should be continued.

Table 2. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurand	As	Ba	Cl^-	Conductivity	Cr	Cu
U_i%	12.2 – **60** %	11.9 – **58** %	10 – **62** %	8 – 33 %	13.6 – **62** %	13.1 – **60** %
Measurand	**DOC**	**F^-**	**Mo**	**Ni**	**pH**	**Sb**
U_i%	16 – **62** %	15 – **74** %	14.5 – **62** %	14.9 – **59** %	2.4 – 15 %	10.5 – **58** %

Measurand	Se	SO_4^{2-}	TDS	V
U_i%	18 – **61** %	10 – **62** %	14 – **65** %	15 – **58** %

[1] In table with bold the values of expanded measurement uncertainty over 50 %.

4 Evaluation of the results

The performance evaluation of the participants was based on the z and E_n scores. The z scores were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 8). The E_n scores were calculated using the assigned values and their uncertainties (Appendix 9).

The z and E_n scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

In total, 85 % of the results evaluated based on z scores were satisfactory when total deviation of 10–35 % and 0.3–0.4 pH units from the assigned values was accepted (Appendix 8). Further, 80 % of the results evaluated based on E_n scores were satisfactory (Appendix 9). Altogether 62 % of participants used accredited analytical methods at least for a part of the measurands, and 87 % of those results (evaluated based on z scores) were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 3. In the previous similar PT, Proftest SYKE 12/2016, 87 % of the results were satisfactory when evaluated with z scores and accepting total deviation of 10–40 % and 0.2–0.3 pH units from the assigned value [11].

Table 3. Summary of the performance evaluation in the proficiency test LT 04/2020.

Sample	Measurand	2 x s_{pt}%	Satisfactory results, %		Remarks
			z	E_n	
RT1LS_2	Metals	25–35	88	78	Only approximate performance evaluation for Sb. The results for Ba and Se were evaluated with E_n scores. In the previous similar PT 12/2016 the performance was satisfactory for 83 % of the results when deviation of 20–40 % from the assigned value was accepted [11].
	Anions	15 – 20	87	–	In the previous similar PT 12/2016 the performance was satisfactory for 82 % of the results when deviation of 15–40 % from the assigned value was accepted [11].
	DOC	25	88	–	In the previous similar PT 12/2016 the performance was satisfactory for 67 % of the results when deviation of 30–40 % from the assigned value was accepted [11].
	TDS	20	75	–	In the previous similar PT 12/2016 the performance was satisfactory for 78 % of the results when deviation of 10–15 % from the assigned value was accepted [11].
	pH	0.4 pH units	67	–	In the previous similar PT 12/2016 the performance was satisfactory for 92 % of the results when deviation of 0.2 pH units from the assigned value was accepted [11].
	Conductivity	15	90	–	Good performance. In the previous similar PT 12/2016 the performance was satisfactory for 84 % of the results [11].
RT1LS_8	pH	0.3 pH units	75	–	In the previous similar PT 12/2016 the performance was satisfactory for 100 % of the results when deviation of 0.3 pH units from the assigned value was accepted [11].
	Conductivity	15	80	–	In the previous similar PT 12/2016 the performance was satisfactory for 88 % of the results [11].
RT1LS10	Metals	25 – 30	89	84	The results for As, Ni and Se were evaluated with E_n scores. In the previous similar PT 12/2016 the performance was satisfactory for 91 % of the results when deviation of 20–35 from the assigned value was accepted [11].
	Anions	10 – 25	84	50	The results for F^- were evaluated with E_n scores. In the previous similar PT 12/2016 the performance was satisfactory for 91 % of the results when deviation of 10–40 % from the assigned value was accepted [11].
	DOC	25	89	–	In the previous similar PT 12/2016 the performance evaluation was based on E_n scores and 44 % of the results were satisfactory [11].
	TDS	15	78	–	In the previous similar PT 12/2016 the performance was satisfactory for 95 % of the results when deviation of 10–15 % from the assigned value was accepted [11].

5 Summary

Proftest SYKE carried out the proficiency test (PT) in cooperation with the KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste sample in May-June 2020 (LT 04/2020). The results of the two stage batch leaching test (EN 12457-3) for samples of treated slag from waste combustion were compared and evaluated. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, SO_4^{2-}, F^-, DOC, pH, conductivity, and TDS. In total, 13 laboratories participated in this PT.

Either the robust mean or the median of the results reported by the participants was chosen to be the assigned value for the measurand. For some measurands the leachability was very low and for many participants close or below the limit of detection/quantification. Thus, the assigned value was not set all measurands in the eluates. The evaluation of the performance was based on the z and E_n scores. The uncertainty for the assigned value was estimated at the 95 % confidence level and it was between 1 % and 12 % for the measurands evaluated with z scores. In this proficiency test 85 % of the results evaluated based on z scores were satisfactory when the deviation of 10–35 % or 0.3–0.4 pH units was accepted from the assigned value at the 95 % confidence interval. Further, 80 % of the results evaluated based on E_n scores were satisfactory.

6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä KVVY Tutkimus Oy:n kanssa pätevyyskokeen touko-kesäkuussa 2020 laboratorioille, jotka tekevät liukoisuustestejä jätteiden kaatopaikka-kelpoisuuden arvioimiseksi (LT 04/2020). Pätevyyskokeessa vertailtiin kaatopaikka-kelpoisuuden selvittämisessä käytettävän 2-vaiheisen ravistelutestin (SFS-EN 12457-3) määritystuloksia jätteenpolton seulotuista pohjakuonanäytteistä. Määritettävät testisuureet olivat metallit (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), Cl^-, SO_4^{2-}, F^-, DOC, pH, sähkönjohtavuus ja TDS. Pätevyyskokeeseen osallistui yhteensä 13 laboratoriota.

Testisuureen vertailuarvona käytettiin osallistujien tulosten robustia keskiarvoa tai niiden mediaania. Joidenkin testisuureiden liukoisuus oli hyvin alhainen ja lähellä tai alle määritys- tai toteamisrajan. Tästä syystä kaikille testisuureille ei voitu asettaa vertailuarvoa. Tuloksia arvioitiin sekä z- että E_n-arvojen avulla. Asetetuille vertailuarvoille laskettiin epävarmuus 95 % luottamusvälillä ja se oli välillä 1–12 % z-arvoilla arvioiduilla testisuureilla. Tässä pätevyys-kokeessa z-arvoilla arvioiduista tuloksista oli hyväksyttäviä 85 %, kun tulosten sallittiin vaihdella 10–35 % tai 0,3–0,4 pH yksikköä vertailuarvosta. E_n-arvoilla arvioiduista tuloksista oli hyväksyttyjä 80 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
Czech Republic	ALS Czech Republic s.r.o.
Finland	Boliden Harjavalta Oy
	EPSE Oy
	Eurofins Ahma Oy, Oulu
	Eurofins Labtium Oy, Kuopio
	Fortum Waste Solutions Oy, Riihimäki
	KVVY Tutkimus Oy, Tampere
	MetropoliLab Oy
	SGS Finland Oy, Kotka
	SYNLAB Analytics & Services Finland Oy
	Umicore Finland Oy
Greece	Athens Analysis Laboratories S.A.
Italy	Geo-Chemic-Lab

APPENDIX 2: Homogeneity of the samples

The homogeneity of the samples was tested by conducting one stage batch leaching test for 4 samples and by analyzing the measurands: Ba, Cr, Cu, Mo, Sb, Zn, V, Cl^-, F^-, DOC, pH, and conductivity.

Criterion for homogeneity:

$$s_{sam}/s_h < 0.5$$

s_h = standard deviation for homogeneity testing
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

Measurand	Concentration [mg/kg]	n	s_{pt} %	s_h %	s_h	s_{sam}	s_{sam}/s_h	s_{sam} / s_h < 0.5 ?
Ba	0.40	4	12.5	10	0.04	0.01	0.253	Yes
Cl^-	5050	4	5 – 7.5	5	253	57.7	0.229	Yes
Conductivity	352	4	7.5	5	17.6	0.50	0.028	Yes
Cr	3.03	4	12.5	10	0.30	0.05	0.165	Yes
Cu	0.69	4	12.5 – 15	10	0.069	0.005	0.073	Yes
DOC	135	4	12.5	12.5	16.9	5.77	0.342	Yes
F^-	5.1	4	-	10	0.51	0.08	0.160	Yes
Mo	1.65	4	12.5 – 15	12.5	0.21	0.06	0.280	Yes
pH	11	4	1.5 – 2	1	0.11	0.000	0.000	Yes
Sb	0.42	4	15 – 17.5	15	0.06	0.03	0.453	Yes
V	0.19	4	12.5	10	0.019	0.005	0.260	Yes

s_{pt} = standard deviation for proficiency assessment

Conclusion: All criteria for homogeneity were fulfilled and the samples could be considered homogenous.

APPENDIX 3: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
6	There was no TDS on the results table. There were too many replicates for Hg on the results table.	The results table was corrected (missing measurand TDS was added) and the participant was thanked for the information. The participants that already had used the result table were informed. The excess replicates for Hg were removed when possible and in cases where removal was not possible, participants were informed.

Participant	Comments to the results	Action / Proftest SYKE
1	The preliminary results report was missing from ProftestWEB.	The participant was thanked for the information and the report was uploaded to ProftestWEB.
10	The participant informed that they had reported all their results of the eluates erroneously.	The provider does not correct the results after the preliminary results report is published. The participant can re-calculate the z and E_n scores according to the Guide for participants [7].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
All	The provider regrets that TDS was missing from the results table and there were too many replicates for Hg. More attention will be paid in the future when preparing the results table.

APPENDIX 4: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt} [1)]
As	RT1LS10	mg/kg	0.024	0.012	49.8	Median	-
Ba	RT1LS_2	mg/kg	0.096	0.023	24.0	Median	-
	RT1LS10	mg/kg	0.42	0.04	8.4	Median	0.34
Cl	RT1LS_2	mg/kg	4726	161	3.4	Median	0.23
	RT1LS10	mg/kg	4975	109	2.2	Median	0.22
Conductivity 25	RT1LS_2	mS/m	1185	53	4.5	Median	0.30
	RT1LS_8	mS/m	198	6	3.2	Median	0.21
Cr	RT1LS_2	mg/kg	2.09	0.10	4.7	Median	0.19
	RT1LS10	mg/kg	2.71	0.14	5.3	Median	0.21
Cu	RT1LS_2	mg/kg	0.47	0.04	9.2	Median	0.31
	RT1LS10	mg/kg	0.74	0.05	7.1	Median	0.28
DOC	RT1LS_2	mg/kg	114	9	7.7	Median	0.31
	RT1LS10	mg/kg	146	10	7.1	Median	0.28
F	RT1LS10	mg/kg	5.34	3.40	63.7	Median	-
Mo	RT1LS_2	mg/kg	1.09	0.08	7.5	Median	0.25
	RT1LS10	mg/kg	1.49	0.07	4.9	Median	0.20
Ni	RT1LS10	mg/kg	0.030	0.023	76.0	Median	-
pH	RT1LS_2		9.78	0.13	1.3	Median	0.33
	RT1LS_8		10.7	0.1	1.0	Median	0.33
Sb	RT1LS_2	mg/kg	0.069	0.008	12.3	Median	0.35
	RT1LS10	mg/kg	0.39	0.04	9.2	Median	0.31
Se	RT1LS_2	mg/kg	0.022	0.012	53.6	Median	-
	RT1LS10	mg/kg	0.052	0.024	45.7	Median	-
SO_4	RT1LS_2	mg/kg	6150	148	2.4	Median	0.12
	RT1LS10	mg/kg	10053	834	8.3	Robust mean	0.33
TDS	RT1LS_2	mg/kg	16594	946	5.7	Median	0.29
	RT1LS10	mg/kg	23228	906	3.9	Median	0.26
V	RT1LS_2	mg/kg	0.034	0.002	7.1	Median	0.28
	RT1LS10	mg/kg	0.17	0.01	5.3	Median	0.21

[1)] Value calculated only for the measurands where the standard deviation for proficiency assessment was set.

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= the standard deviation for proficiency assessment
u_{pt}= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 5: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participant's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n_{stat}	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i ($i = 1, 2, \ldots, p$)
s^* = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i ($i = 1, 2, \ldots, p$):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [3].

APPENDIX 6: Results of each participant

Participant 1												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*<0.06*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		*<0.3*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.090	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		-1.14	0.42	25	0.36	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*< 0.004*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*< 0.02*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		-0.36	4726	15	4600	4726	4753	253	5.3	10
	mg/kg	RT1LS10		0.10	4975	10	5000	4975	4995	173	3.5	10
Cr	mg/kg	RT1LS_2		-0.34	2.09	25	2.00	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		-0.03	2.71	25	2.70	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		1.84	0.47	30	0.60	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		1.73	0.74	25	0.90	0.74	0.74	0.09	11.7	11
Hg	mg/kg	RT1LS_2					*< 0.004*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*< 0.02*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		-0.55	1.09	30	1.00	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		-0.48	1.49	25	1.40	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*< 0.004*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*< 0.02*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*< 0.02*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*< 0.1*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-1.94	9.78	4	9.40	9.78	9.77	0.16	1.7	7
		RT1LS_8		0.00	10.7	3	10.7	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		1.74	0.069	35	0.090	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		0.85	0.39	30	0.44	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*< 0.02*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*< 0.1*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		0.08	6150	20	6200	6150	6119	219	3.6	9
	mg/kg	RT1LS10		0.75	10053	25	11000	10105	9984	1162	11.6	12
V	mg/kg	RT1LS_2		-0.94	0.034	25	0.030	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		0.00	0.17	25	0.17	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*< 0.02*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*< 0.1*	0.12	0.12	0.08	65.6	2

Participant 2												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS10			0.024		*<0.1*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS10		-0.38	0.42	25	0.40	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS10					*<0.02*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS10		-0.62	4975	10	4820	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		0.45	1185	15	1225	1185	1172	79	6.7	9
	mS/m	RT1LS_8		3.30	198	15	247	198	197	9	4.5	8
Cr	mg/kg	RT1LS10		1.45	2.71	25	3.20	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS10		-0.65	0.74	25	0.68	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS10		0.22	146	25	150	146	151	15	10.1	8
F	mg/kg	RT1LS10			5.34		14.00	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS10					*<0.01*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS10		1.13	1.49	25	1.70	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS10			0.030		*<0.1*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS10					*<0.1*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-2.97	9.78	4	9.20	9.78	9.77	0.16	1.7	7
		RT1LS_8		-2.49	10.7	3	10.3	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS10		-3.08	0.39	30	0.21	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS10			0.052		*<0.1*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS10		1.34	10053	25	11740	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS10		3.46	23228	15	29250	23228	23511	1203	5.1	7
V	mg/kg	RT1LS10		-0.94	0.17	25	0.15	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS10					*<0.1*	0.12	0.12	0.08	65.6	2

Participant 3												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
Cr	mg/kg	RT1LS_2		0.11	2.09	25	2.12	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		0.12	2.71	25	2.75	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		-1.13	0.47	30	0.39	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		-1.62	0.74	25	0.59	0.74	0.74	0.09	11.7	11
Mo	mg/kg	RT1LS_2		-0.18	1.09	30	1.06	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		-0.48	1.49	25	1.40	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					0.080	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		0.060	0.030	0.031	0.024	76.0	4
SO_4	mg/kg	RT1LS_2		0.16	6150	20	6246	6150	6119	219	3.6	9
	mg/kg	RT1LS10		0.11	10053	25	10185	10105	9984	1162	11.6	12

Participant 4												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*<0.05*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		*<0.05*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.188	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		1.47	0.42	25	0.50	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.02*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*<0.02*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		0.52	4726	15	4910	4726	4753	253	5.3	10
	mg/kg	RT1LS10		0.18	4975	10	5020	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		0.06	1185	15	1190	1185	1172	79	6.7	9
	mS/m	RT1LS_8		0.07	198	15	199	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		0.19	2.09	25	2.14	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		-0.15	2.71	25	2.66	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		-0.13	0.47	30	0.46	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		-0.51	0.74	25	0.69	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		-0.35	114	25	109	114	116	12	10.2	7
	mg/kg	RT1LS10		-0.55	146	25	136	146	151	15	10.1	8
F	mg/kg	RT1LS_2					*<2*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		*<4.1*	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*<0.005*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*<0.005*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		0.86	1.09	30	1.23	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		0.48	1.49	25	1.58	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*<0.05*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*<0.05*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<0.05*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<0.05*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		0.00	9.78	4	9.78	9.78	9.77	0.16	1.7	7
		RT1LS_8		0.62	10.7	3	10.8	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		-0.46	0.069	35	0.063	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		-0.12	0.39	30	0.38	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*<0.05*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*<0.05*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		0.00	6150	20	6150	6150	6119	219	3.6	9
	mg/kg	RT1LS10		0.00	10053	25	10050	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		0.79	16594	20	17900	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		0.90	23228	15	24800	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2			0.034	25	*<0.05*	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		-0.09	0.17	25	0.17	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*<0.05*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*<0.05*	0.12	0.12	0.08	65.6	2

Participant 5												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*< 0.006*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		0.024	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.089	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		-1.09	0.42	25	0.36	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*< 0.006*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*< 0.024*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		0.36	4726	15	4852	4726	4753	253	5.3	10
	mg/kg	RT1LS10		4.68	4975	10	6138	4975	4995	173	3.5	10
Cr	mg/kg	RT1LS_2		-0.69	2.09	25	1.91	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		0.71	2.71	25	2.95	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		-1.04	0.47	30	0.40	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		-0.01	0.74	25	0.74	0.74	0.74	0.09	11.7	11
F	mg/kg	RT1LS_2					2.20	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		5.34	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*<0.001*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*< 0.004*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		-0.73	1.09	30	0.97	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		0.00	1.49	25	1.49	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					0.006	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		0.006	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*< 0.006*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*< 0.024*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-4.86	9.78	4	8.83	9.78	9.77	0.16	1.7	7
		RT1LS_8		-13.58	10.7	3	8.5	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		1.90	0.069	35	0.092	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		0.89	0.39	30	0.44	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		0.022	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		0.022	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-0.07	6150	20	6106	6150	6119	219	3.6	9
	mg/kg	RT1LS10		1.15	10053	25	11500	10105	9984	1162	11.6	12
V	mg/kg	RT1LS_2		0.47	0.034	25	0.036	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		-0.42	0.17	25	0.16	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*< 0.003*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*< 0.024*	0.12	0.12	0.08	65.6	2

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*< 0.1*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		*< 0.1*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		*<4.0*	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10			0.42	25	*< 4.0*	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*< 0.01*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*< 0.01*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		-0.90	4726	15	4408	4726	4753	253	5.3	10
	mg/kg	RT1LS10		0.21	4975	10	5026	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		-1.91	1185	15	1015	1185	1172	79	6.7	9
	mS/m	RT1LS_8		-0.07	198	15	197	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		-0.96	2.09	25	1.84	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		-0.53	2.71	25	2.53	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2			0.47	30	*< 0.4*	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		-0.54	0.74	25	0.69	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		-0.77	114	25	103	114	116	12	10.2	7
	mg/kg	RT1LS10		-0.27	146	25	141	146	151	15	10.1	8
F	mg/kg	RT1LS_2					*< 2*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		*< 5*	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*< 0.002*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*< 0.002*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		-0.55	1.09	30	1.00	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		-0.70	1.49	25	1.36	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*< 0.1*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*< 0.1*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*< 0.1*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*< 0.1*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-1.48	9.78	4	9.49	9.78	9.77	0.16	1.7	7
		RT1LS_8		-1.50	10.7	3	10.5	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		-1.57	0.069	35	0.050	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		-0.68	0.39	30	0.35	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*< 0.03*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		0.050	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-1.50	6150	20	5227	6150	6119	219	3.6	9
	mg/kg	RT1LS10		-0.82	10053	25	9023	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		-0.87	16594	20	15157	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		-0.15	23228	15	22962	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2			0.034	25	*< 0.4*	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10			0.17	25	*< 0.4*	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*< 0.8*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*< 0.8*	0.12	0.12	0.08	65.6	2

Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					0.006	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		0.014	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.102	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		0.23	0.42	25	0.43	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.001*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*<0.005*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		-0.38	4726	15	4590	4726	4753	253	5.3	10
	mg/kg	RT1LS10		-0.10	4975	10	4950	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		0.83	1185	15	1259	1185	1172	79	6.7	9
	mS/m	RT1LS_8		-0.88	198	15	185	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		0.08	2.09	25	2.11	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		0.00	2.71	25	2.71	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		0.64	0.47	30	0.52	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		0.92	0.74	25	0.83	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		0.49	114	25	121	114	116	12	10.2	7
	mg/kg	RT1LS10		1.42	146	25	172	146	151	15	10.1	8
F	mg/kg	RT1LS_2					*<1*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		*<5*	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*<0.001*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*<0.004*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		1.28	1.09	30	1.30	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		0.70	1.49	25	1.62	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					0.004	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*<0.01*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<0.002*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<0.01*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		1.12	9.78	4	10.00	9.78	9.77	0.16	1.7	7
		RT1LS_8		0.00	10.7	3	10.7	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		-0.84	0.069	35	0.059	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		-0.15	0.39	30	0.38	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		0.017	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*<0.04*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-0.07	6150	20	6110	6150	6119	219	3.6	9
	mg/kg	RT1LS10		0.09	10053	25	10160	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		0.37	16594	20	17200	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		0.67	23228	15	24400	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2		0.47	0.034	25	0.036	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		0.09	0.17	25	0.17	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*<0.01*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*<0.05*	0.12	0.12	0.08	65.6	2

Participant 8												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					0.006	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		0.014	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.091	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		-1.18	0.42	25	0.36	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.001*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*<0.005*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		0.51	4726	15	4906	4726	4753	253	5.3	10
	mg/kg	RT1LS10		-0.16	4975	10	4935	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		-0.06	1185	15	1180	1185	1172	79	6.7	9
	mS/m	RT1LS_8		0.34	198	15	203	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		0.77	2.09	25	2.29	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		-0.09	2.71	25	2.68	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		-0.06	0.47	30	0.47	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		-0.58	0.74	25	0.69	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		0.00	114	25	114	114	116	12	10.2	7
	mg/kg	RT1LS10		-0.38	146	25	139	146	151	15	10.1	8
F	mg/kg	RT1LS_2					0.73	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		6.55	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					0.000	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*<0.0001*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		0.24	1.09	30	1.13	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		-0.64	1.49	25	1.37	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*<0.006*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*<0.03*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<0.002*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<0.01*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		0.10	9.78	4	9.80	9.78	9.77	0.16	1.7	7
		RT1LS_8		-0.62	10.7	3	10.6	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		-0.33	0.069	35	0.065	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		-0.29	0.39	30	0.37	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		0.021	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*<0.06*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		0.10	6150	20	6210	6150	6119	219	3.6	9
	mg/kg	RT1LS10		-0.51	10053	25	9418	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		-0.55	16594	20	15680	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		-0.80	23228	15	21837	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2		0.73	0.034	25	0.037	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		0.05	0.17	25	0.17	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					0.016	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					0.17	0.12	0.12	0.08	65.6	2

Participant 9												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					0.040	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		0.048	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.134	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		6.69	0.42	25	0.77	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					0.036	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					0.037	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		-0.74	4726	15	4462	4726	4753	253	5.3	10
	mg/kg	RT1LS10		-0.17	4975	10	4933	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		-0.70	1185	15	1123	1185	1172	79	6.7	9
	mS/m	RT1LS_8		-0.40	198	15	192	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		0.83	2.09	25	2.31	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		1.11	2.71	25	3.09	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		0.26	0.47	30	0.49	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		0.81	0.74	25	0.82	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		-0.72	114	25	104	114	116	12	10.2	7
	mg/kg	RT1LS10		-0.22	146	25	142	146	151	15	10.1	8
F	mg/kg	RT1LS_2					0.28	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		1.43	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					0.035	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					0.035	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		0.33	1.09	30	1.14	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		0.28	1.49	25	1.54	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					0.038	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		0.040	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					0.035	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					0.037	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-0.41	9.78	4	9.70	9.78	9.77	0.16	1.7	7
		RT1LS_8		-0.62	10.7	3	10.6	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		0.83	0.069	35	0.079	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		1.08	0.39	30	0.45	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		0.049	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		0.053	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-2.90	6150	20	4367	6150	6119	219	3.6	9
	mg/kg	RT1LS10		-2.03	10053	25	7496	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		-0.37	16594	20	15987	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		0.00	23228	15	23228	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2		7.29	0.034	25	0.065	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		1.08	0.17	25	0.19	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					0.040	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					0.06	0.12	0.12	0.08	65.6	2

Participant 10												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					0.002	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		0.025	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.068	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		0.19	0.42	25	0.43	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.0002*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					0.003	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		-12.20	4726	15	401	4726	4753	253	5.3	10
	mg/kg	RT1LS10		64.44	4975	10	21005	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		-11.02	1185	15	206	1185	1172	79	6.7	9
	mS/m	RT1LS_8		63.97	198	15	1148	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		-6.93	2.09	25	0.28	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		19.16	2.71	25	9.20	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		-5.39	0.47	30	0.09	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		12.54	0.74	25	1.90	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		-6.91	114	25	16	114	116	12	10.2	7
	mg/kg	RT1LS10		20.66	146	25	523	146	151	15	10.1	8
F	mg/kg	RT1LS_2					*<0.2*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		*<1.0*	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					0.001	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					0.009	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		-5.81	1.09	30	0.14	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		18.31	1.49	25	4.90	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*<0.001*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		0.019	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<0.001*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<0.006*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		3.68	9.78	4	10.50	9.78	9.77	0.16	1.7	7
		RT1LS_8		-7.48	10.7	3	9.5	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		0.58	0.069	35	0.076	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		-2.22	0.39	30	0.26	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*<0.006*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		0.079	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-7.95	6150	20	1259	6150	6119	219	3.6	9
	mg/kg	RT1LS10		12.57	10053	25	25850	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		-8.38	16594	20	2695	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		30.62	23228	15	76570	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2		-0.47	0.034	25	0.032	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		0.47	0.17	25	0.18	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*<0.024*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*<0.12*	0.12	0.12	0.08	65.6	2

Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*<0.020*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		*<0.10*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.703	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		16.00	0.42	25	1.26	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.0020*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*<0.010*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		1.17	4726	15	5140	4726	4753	253	5.3	10
	mg/kg	RT1LS10		1.67	4975	10	5390	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		-0.84	1185	15	1110	1185	1172	79	6.7	9
	mS/m	RT1LS_8		0.47	198	15	205	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		-0.11	2.09	25	2.06	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		-0.03	2.71	25	2.70	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		-0.03	0.47	30	0.47	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		0.05	0.74	25	0.75	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		1.40	114	25	134	114	116	12	10.2	7
	mg/kg	RT1LS10		1.64	146	25	176	146	151	15	10.1	8
F	mg/kg	RT1LS_2					*<2.0*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		*<10*	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*<0.00020*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*<0.0010*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		0.00	1.09	30	1.09	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		0.00	1.49	25	1.49	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*<0.010*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*<0.050*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<0.020*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<0.10*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		0.61	9.78	4	9.90	9.78	9.77	0.16	1.7	7
		RT1LS_8		0.62	10.7	3	10.8	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		0.27	0.069	35	0.072	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		0.46	0.39	30	0.42	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*<0.020*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*<0.10*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-0.29	6150	20	5970	6150	6119	219	3.6	9
	mg/kg	RT1LS10		-0.11	10053	25	9920	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		0.73	16594	20	17800	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		0.96	23228	15	24900	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2		-0.54	0.034	25	0.032	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		0.05	0.17	25	0.17	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*<0.010*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*<0.050*	0.12	0.12	0.08	65.6	2

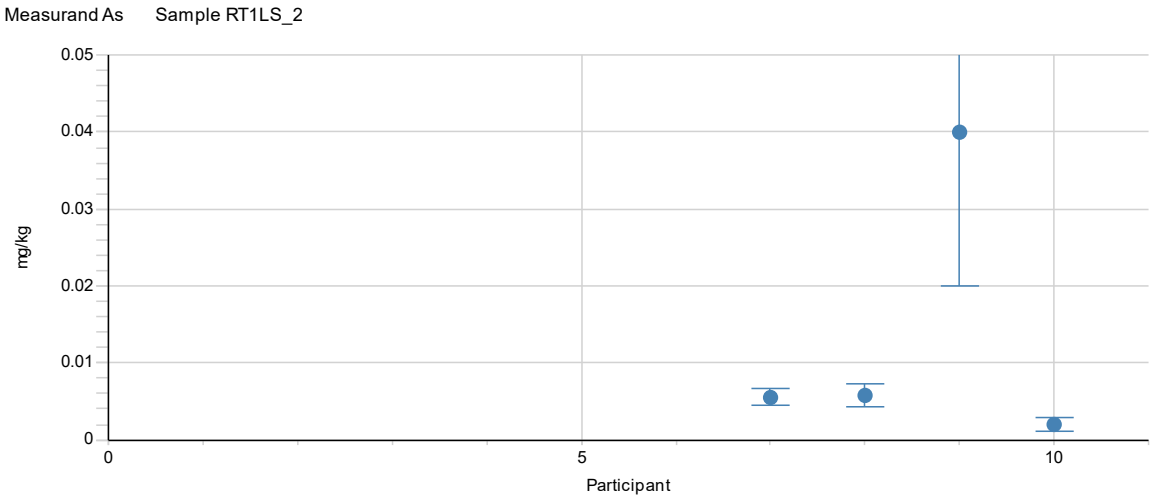
Participant 12												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*<1*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		*<1*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		*<1*	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10			0.42	25	*<1*	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.2*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*<0.2*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		-0.36	4726	15	4600	4726	4753	253	5.3	10
	mg/kg	RT1LS10		-0.88	4975	10	4756	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		0.00	1185	15	1185	1185	1172	79	6.7	9
	mS/m	RT1LS_8		-0.74	198	15	187	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		-0.57	2.09	25	1.94	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		-0.41	2.71	25	2.57	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2			0.47	30	*<1*	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10			0.74	25	*<1*	0.74	0.74	0.09	11.7	11
F	mg/kg	RT1LS_2					*<1*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		5.10	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*<0.001*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*<0.001*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		-0.73	1.09	30	0.97	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		-1.02	1.49	25	1.30	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*<1*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*<1*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<1*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<1*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-0.41	9.78	4	9.70	9.78	9.77	0.16	1.7	7
		RT1LS_8		0.62	10.7	3	10.8	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		32.38	0.069	35	0.460	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		7.01	0.39	30	0.80	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*<0.5*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*<0.5*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		-0.83	6150	20	5640	6150	6119	219	3.6	9
	mg/kg	RT1LS10		-0.79	10053	25	9056	10105	9984	1162	11.6	12
V	mg/kg	RT1LS_2			0.034	25	*<1*	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10			0.17	25	*<1*	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*<1*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*<1*	0.12	0.12	0.08	65.6	2

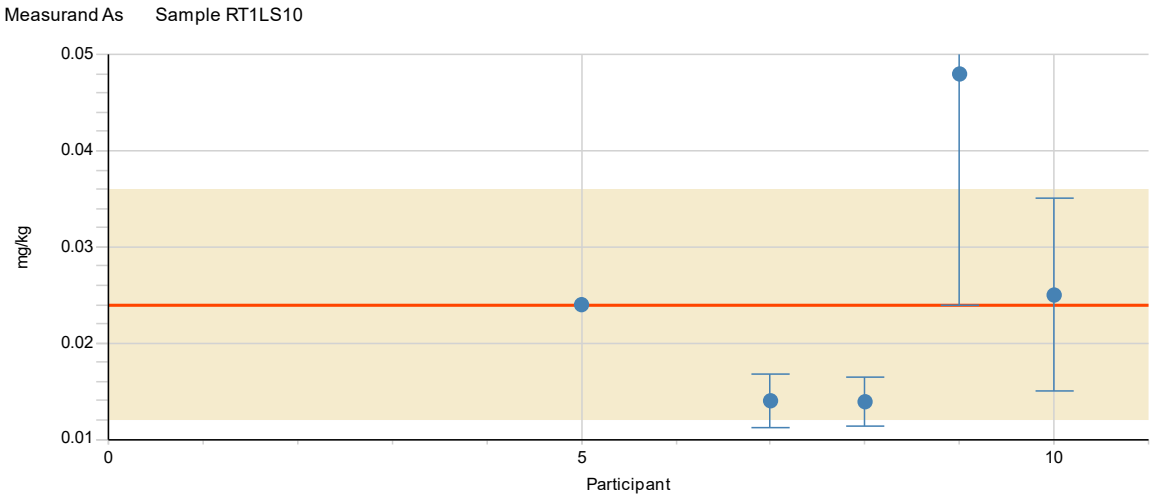
Participant 13												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
As	mg/kg	RT1LS_2					*<0.05*	0.006	0.013	0.018	134.2	4
	mg/kg	RT1LS10			0.024		*<0.05*	0.024	0.025	0.014	55.7	5
Ba	mg/kg	RT1LS_2			0.096		0.120	0.096	0.110	0.037	33.9	8
	mg/kg	RT1LS10		0.19	0.42	25	0.43	0.42	0.41	0.05	11.8	8
Cd	mg/kg	RT1LS_2					*<0.02*	0.036	0.036	0.000	0.0	1
	mg/kg	RT1LS10					*<0.02*	0.020	0.020	0.024	120.2	2
Cl	mg/kg	RT1LS_2		0.93	4726	15	5057	4726	4753	253	5.3	10
	mg/kg	RT1LS10		0.58	4975	10	5119	4975	4995	173	3.5	10
Conductivity 25	mS/m	RT1LS_2		0.84	1185	15	1260	1185	1172	79	6.7	9
	mS/m	RT1LS_8		0.81	198	15	210	198	197	9	4.5	8
Cr	mg/kg	RT1LS_2		2.95	2.09	25	2.86	2.09	2.07	0.15	7.4	10
	mg/kg	RT1LS10		1.83	2.71	25	3.33	2.71	2.82	0.26	9.1	12
Cu	mg/kg	RT1LS_2		0.99	0.47	30	0.54	0.47	0.48	0.07	13.8	9
	mg/kg	RT1LS10		0.65	0.74	25	0.80	0.74	0.74	0.09	11.7	11
DOC	mg/kg	RT1LS_2		0.91	114	25	127	114	116	12	10.2	7
	mg/kg	RT1LS10		0.22	146	25	150	146	151	15	10.1	8
F	mg/kg	RT1LS_2					*<10*	0.73	1.07	1.00	93.7	3
	mg/kg	RT1LS10			5.34		*<10*	5.34	6.48	4.62	71.2	5
Hg	mg/kg	RT1LS_2					*<0.01*	0.001	0.012	0.020	168.0	3
	mg/kg	RT1LS10					*<0.01*	0.022	0.022	0.018	83.6	2
Mo	mg/kg	RT1LS_2		1.77	1.09	30	1.38	1.09	1.12	0.14	12.4	11
	mg/kg	RT1LS10		0.75	1.49	25	1.63	1.49	1.49	0.13	8.5	12
Ni	mg/kg	RT1LS_2					*<0.05*	0.022	0.032	0.036	111.2	4
	mg/kg	RT1LS10			0.030		*<0.05*	0.030	0.031	0.024	76.0	4
Pb	mg/kg	RT1LS_2					*<0.05*	0.035	0.035	0.000	0.0	1
	mg/kg	RT1LS10					*<0.05*	0.037	0.037	0.000	0.0	1
pH		RT1LS_2		-3.02	9.78	4	9.19	9.78	9.77	0.16	1.7	7
		RT1LS_8		0.00	10.7	3	10.7	10.7	10.6	0.2	1.5	10
Sb	mg/kg	RT1LS_2		-0.75	0.069	35	0.060	0.069	0.071	0.014	19.4	10
	mg/kg	RT1LS10		0.00	0.39	30	0.39	0.39	0.39	0.06	14.5	10
Se	mg/kg	RT1LS_2			0.022		*<0.06*	0.022	0.027	0.015	53.6	4
	mg/kg	RT1LS10			0.052		*<0.06*	0.052	0.051	0.023	45.7	4
SO_4	mg/kg	RT1LS_2		0.47	6150	20	6436	6150	6119	219	3.6	9
	mg/kg	RT1LS10		0.16	10053	25	10260	10105	9984	1162	11.6	12
TDS	mg/kg	RT1LS_2		3.53	16594	20	22453	16594	16621	1165	7.0	6
	mg/kg	RT1LS10		-0.44	23228	15	22453	23228	23511	1203	5.1	7
V	mg/kg	RT1LS_2			0.034	25	*<0.1*	0.034	0.034	0.003	8.6	6
	mg/kg	RT1LS10		1.41	0.17	25	0.20	0.17	0.17	0.01	8.3	10
Zn	mg/kg	RT1LS_2					*<0.3*	0.028	0.028	0.017	61.3	2
	mg/kg	RT1LS10					*<0.3*	0.12	0.12	0.08	65.6	2

APPENDIX 7: Results of participants and their uncertainties

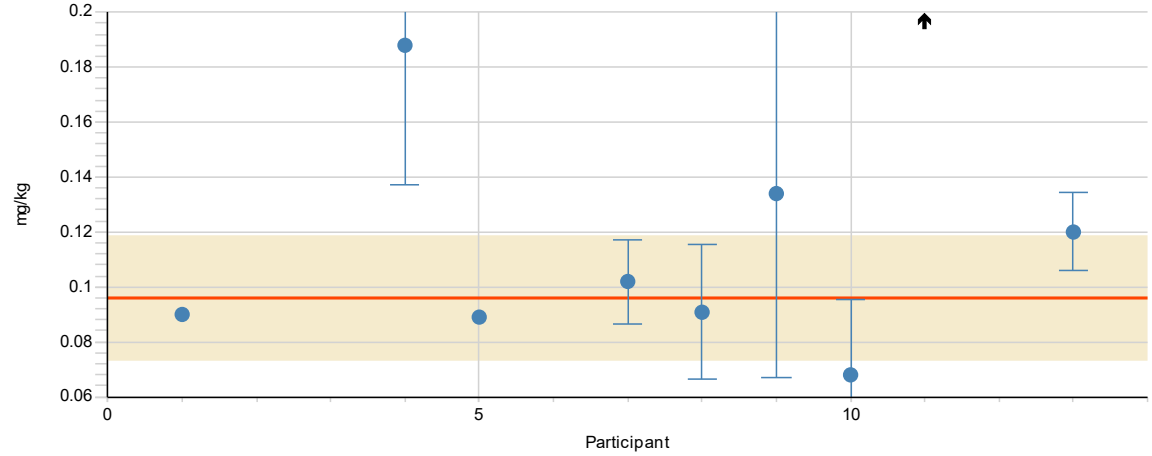
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

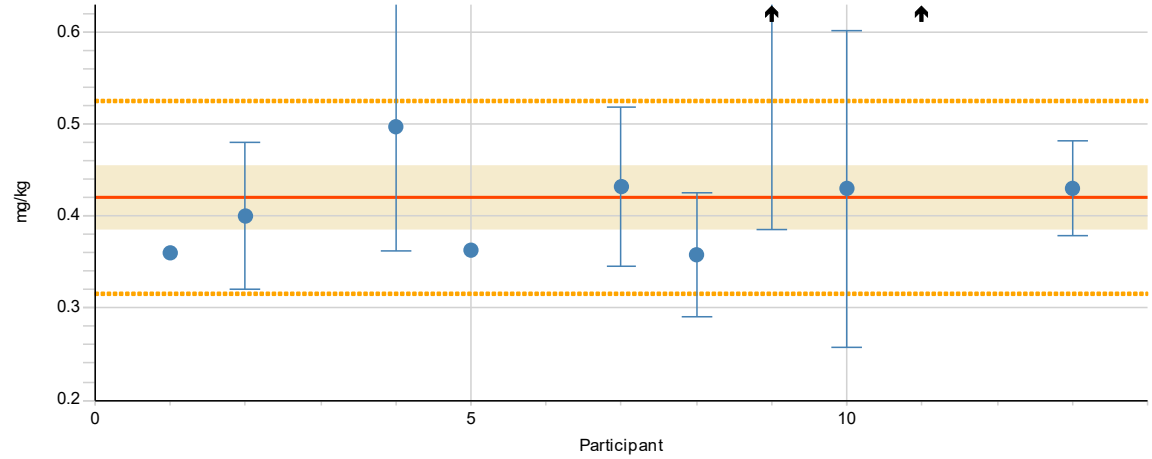




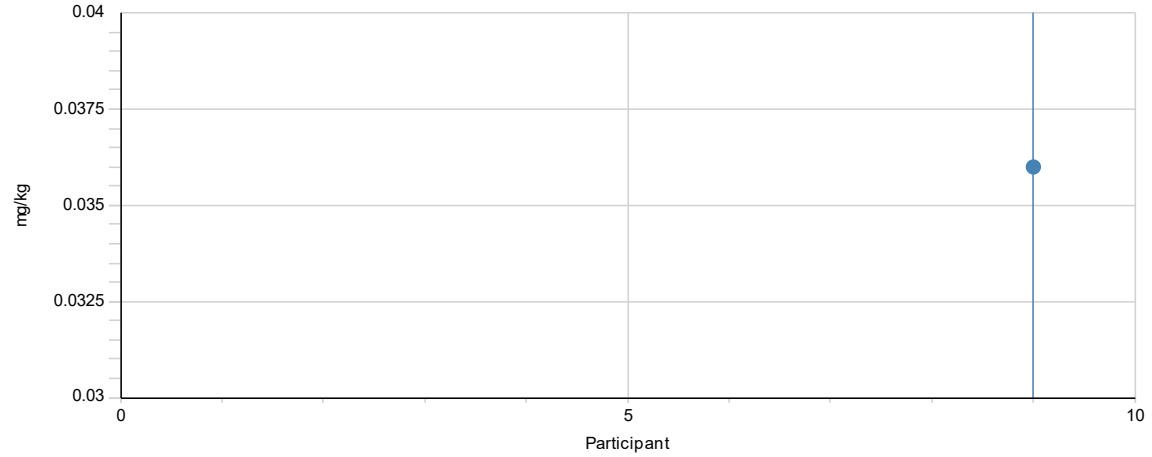
Measurand Ba Sample RT1LS_2



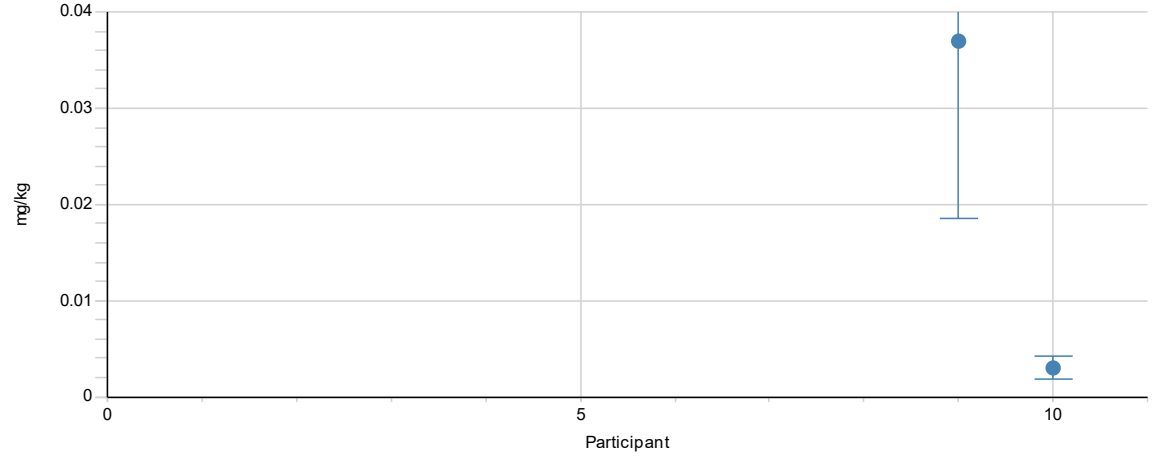
Measurand Ba Sample RT1LS10



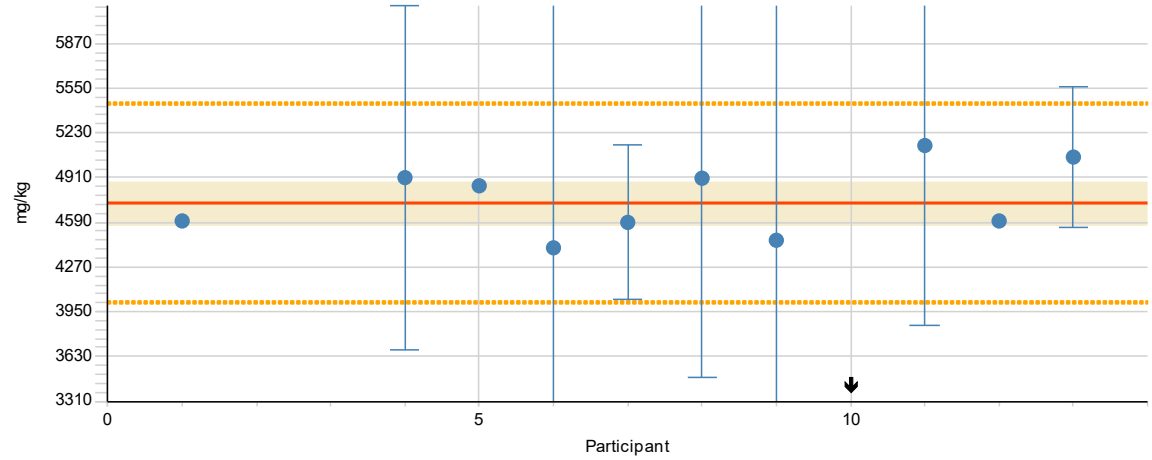
Measurand Cd Sample RT1LS_2



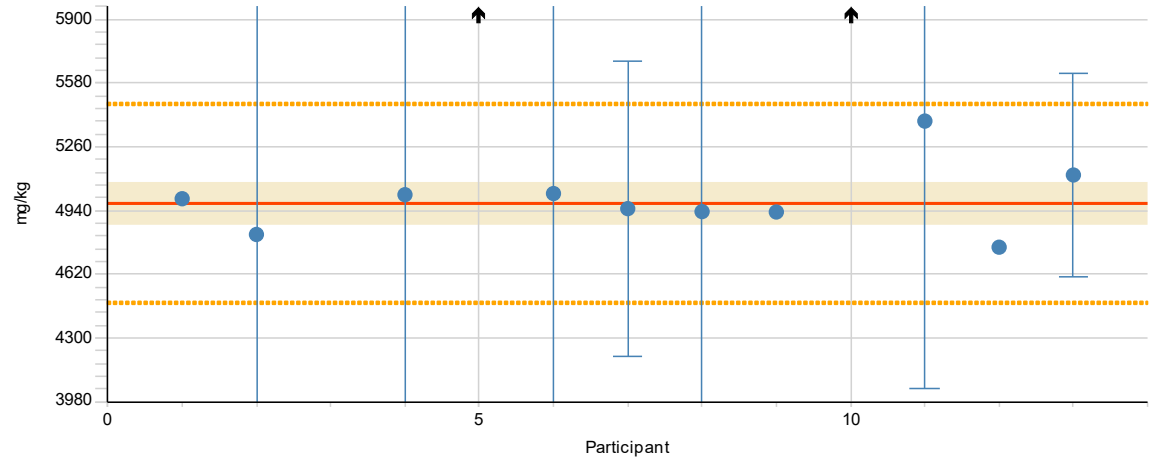
Measurand Cd Sample RT1LS10



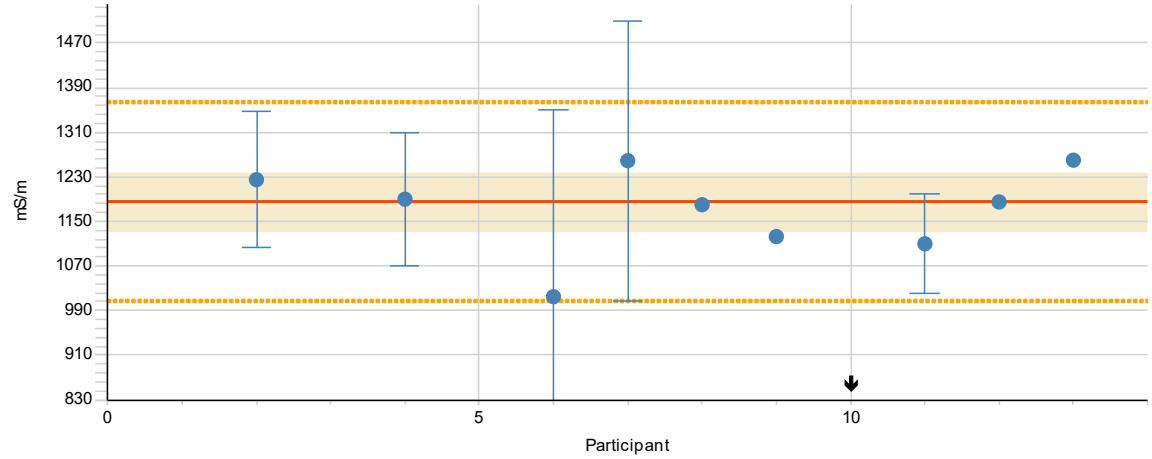
Measurand Cl Sample RT1LS_2



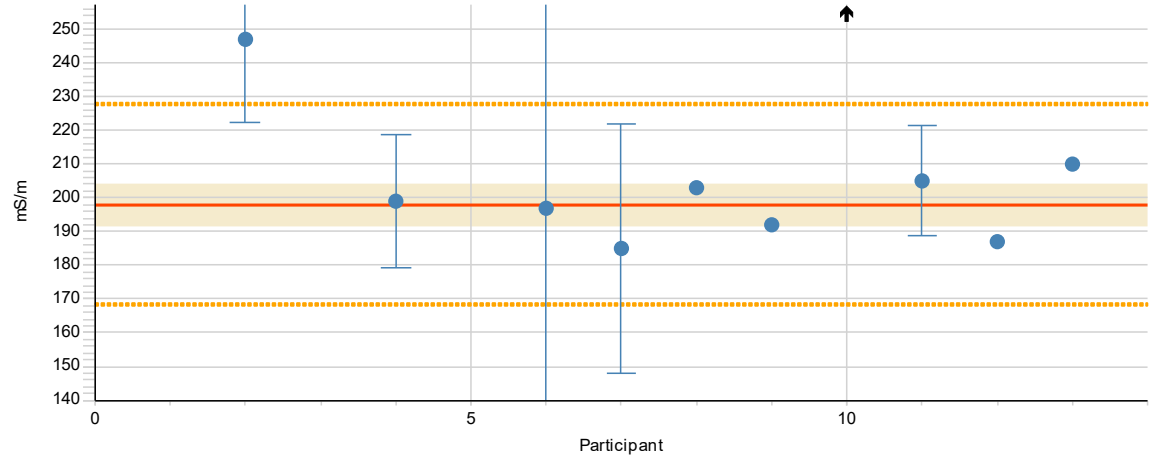
Measurand Cl Sample RT1LS10



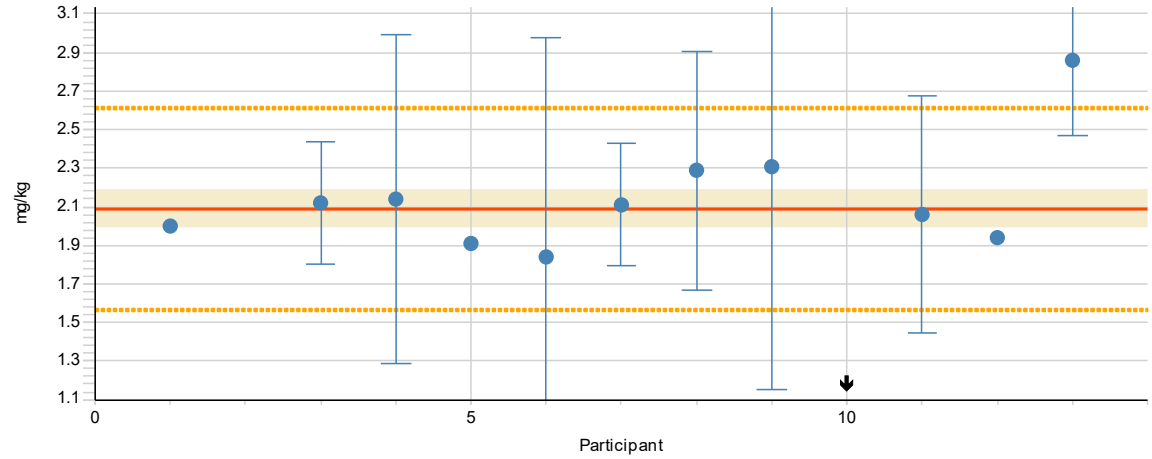
Measurand Conductivity 25 Sample RT1LS_2



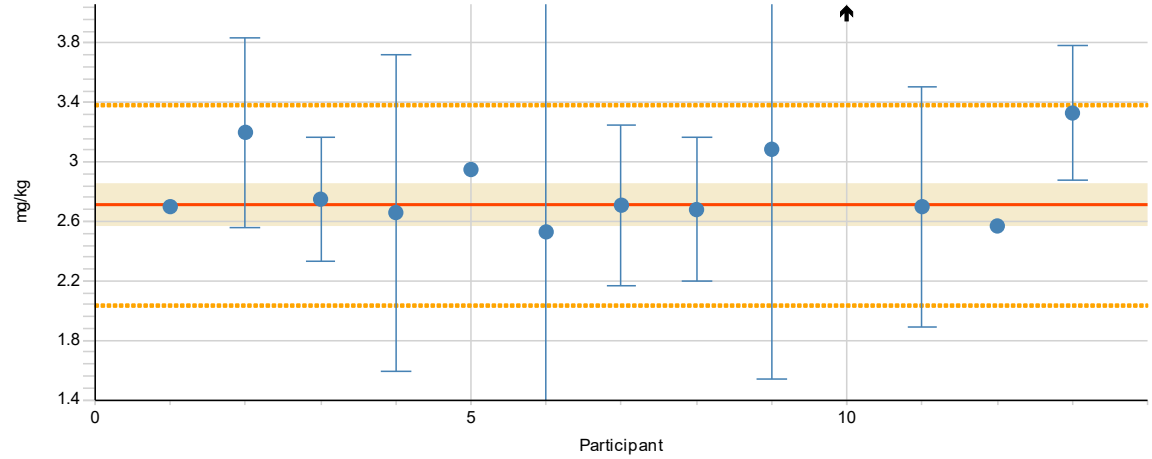
Measurand Conductivity 25 Sample RT1LS_8



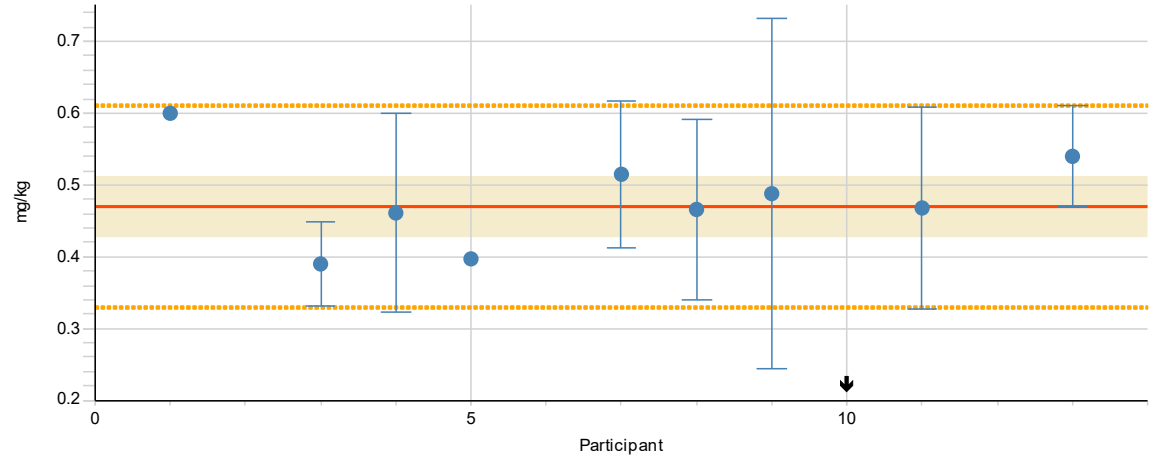
Measurand Cr Sample RT1LS_2



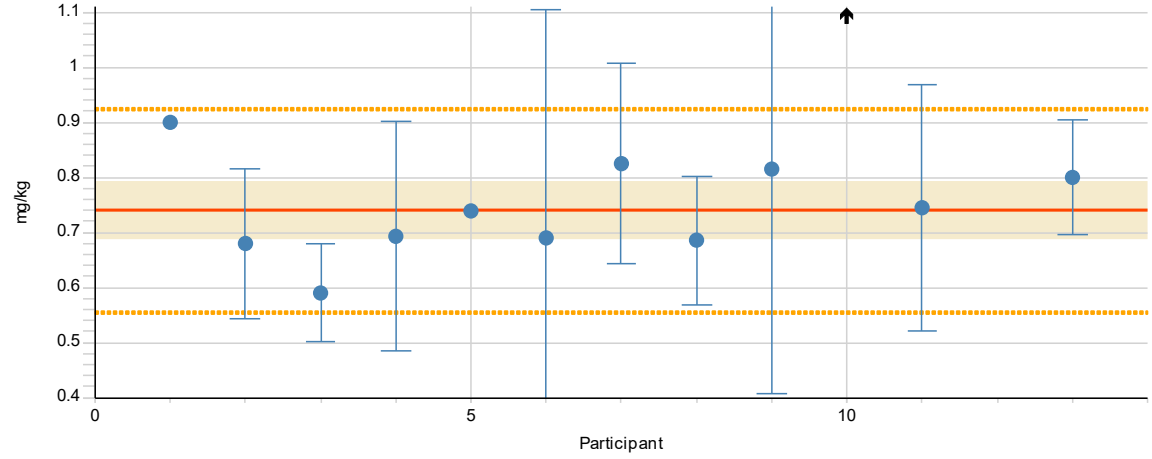
Measurand Cr Sample RT1LS10



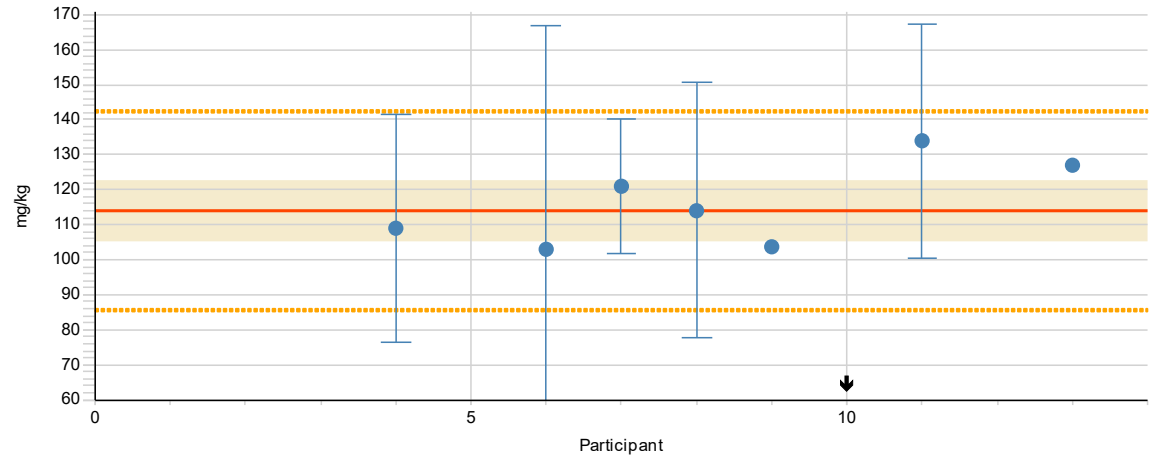
Measurand Cu Sample RT1LS_2



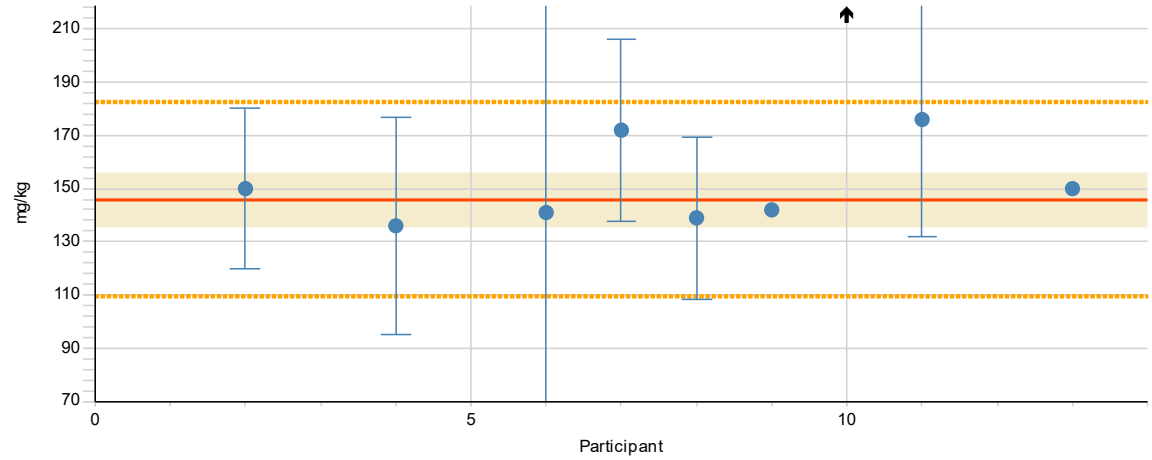
Measurand Cu Sample RT1LS10



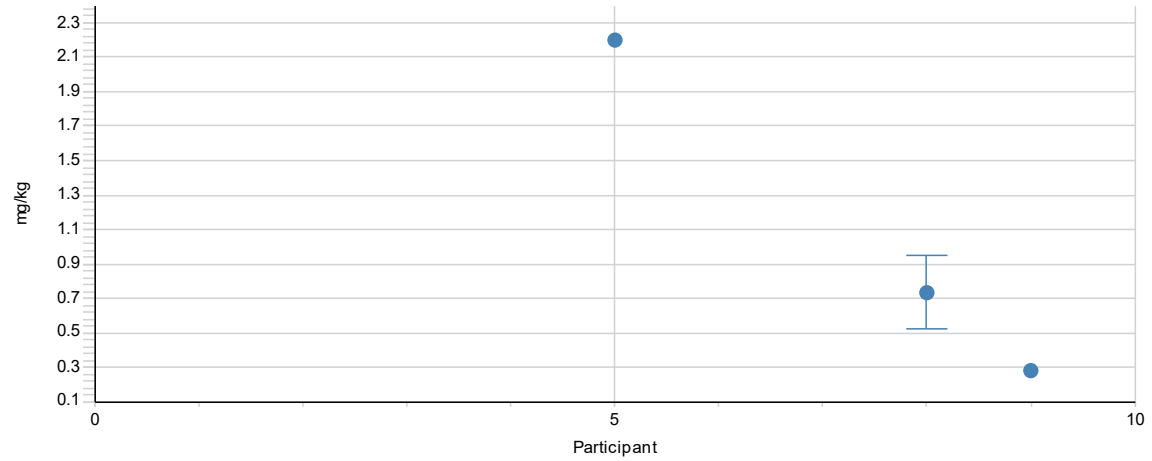
Measurand DOC Sample RT1LS_2



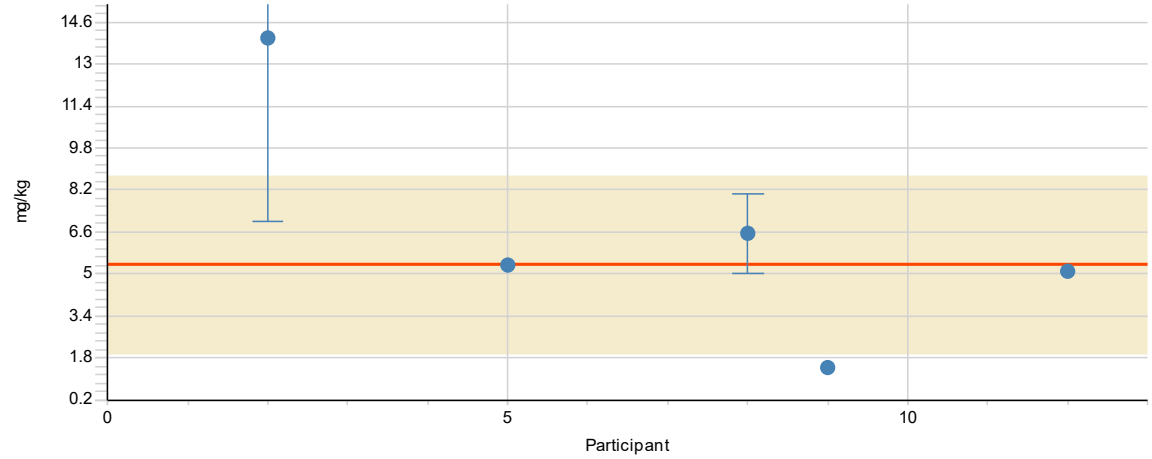
Measurand DOC Sample RT1LS10



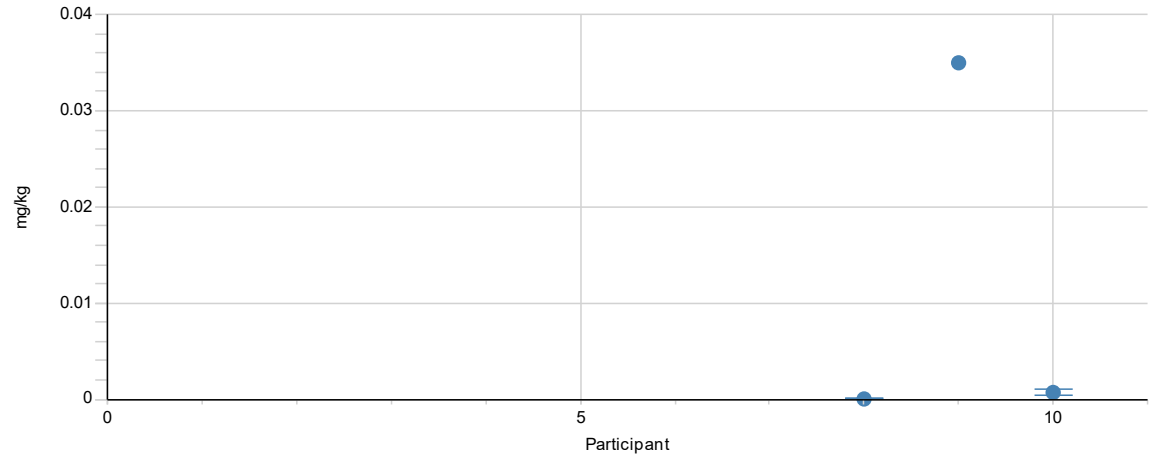
Measurand F Sample RT1LS_2



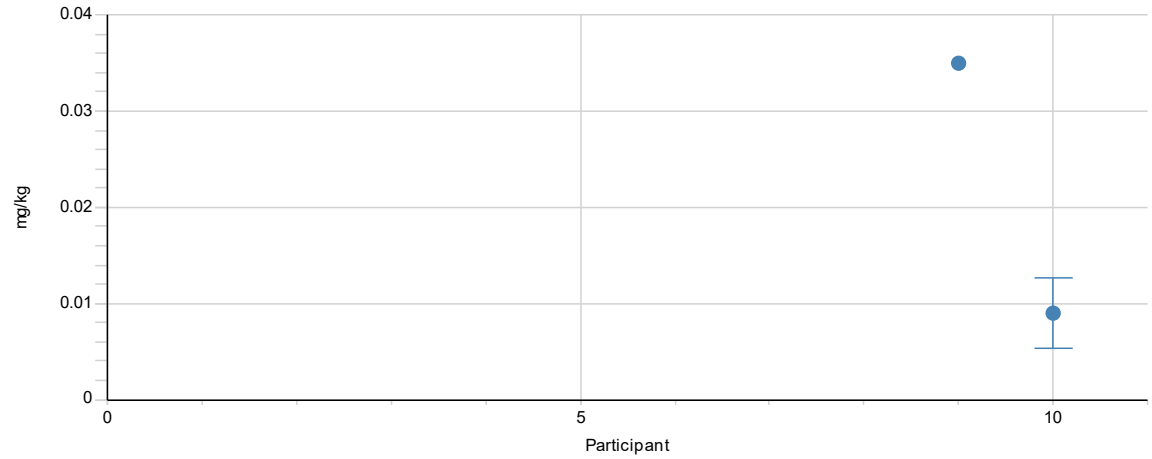
Measurand F Sample RT1LS10



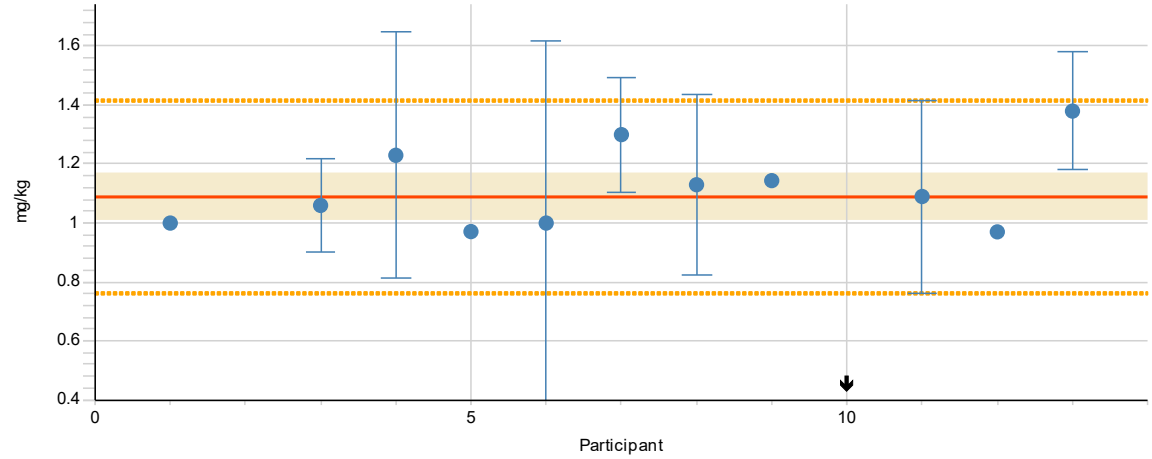
Measurand Hg Sample RT1LS_2



Measurand Hg Sample RT1LS10



Measurand Mo Sample RT1LS_2



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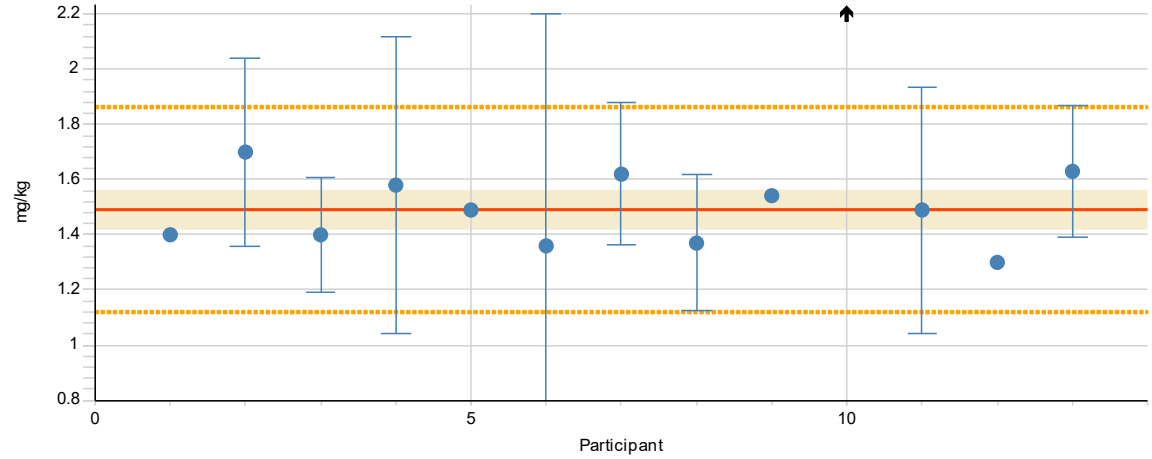
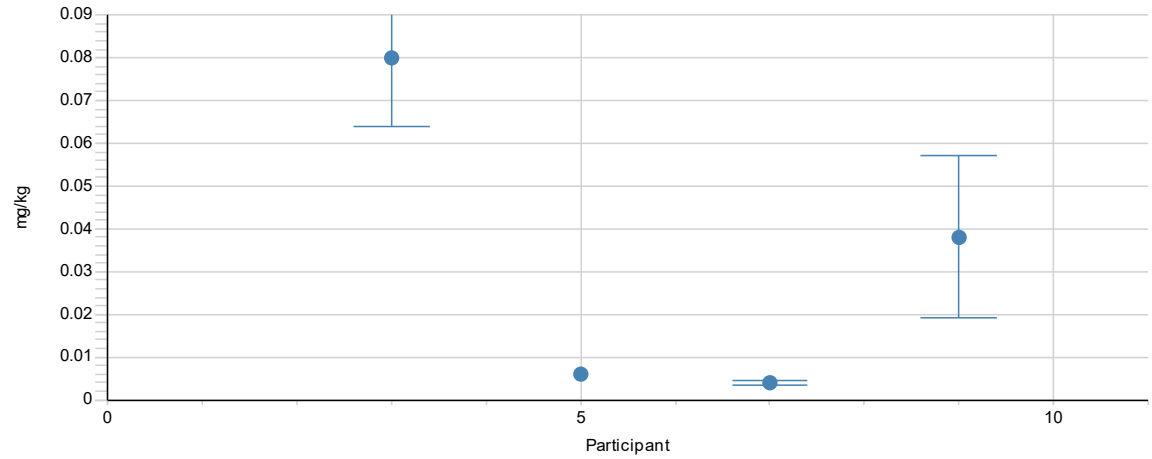
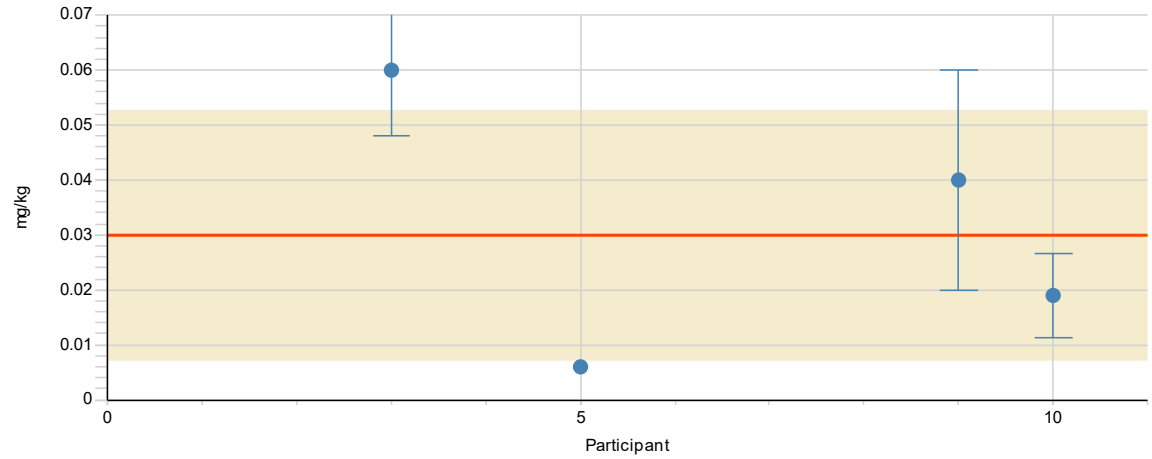


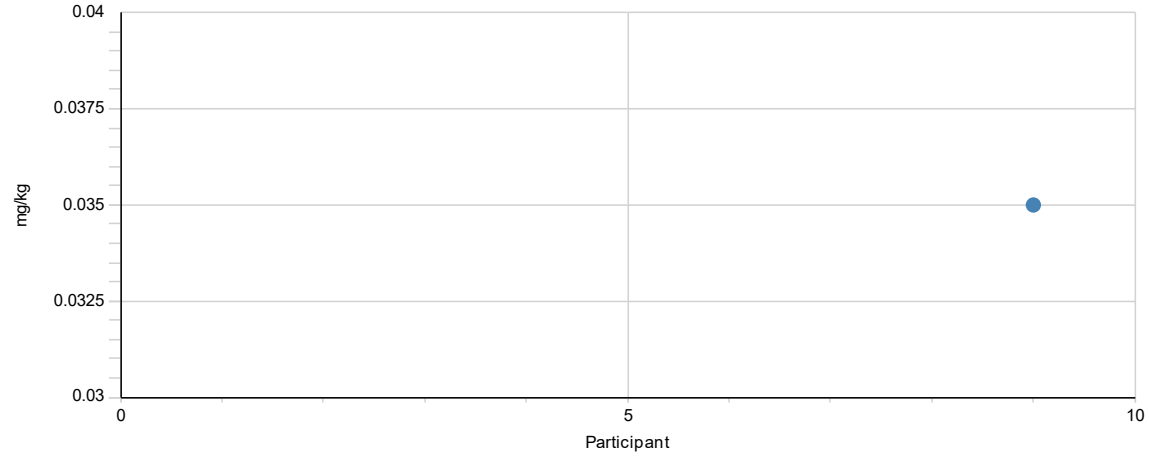
Measurand Ni Sample RT1LS_2



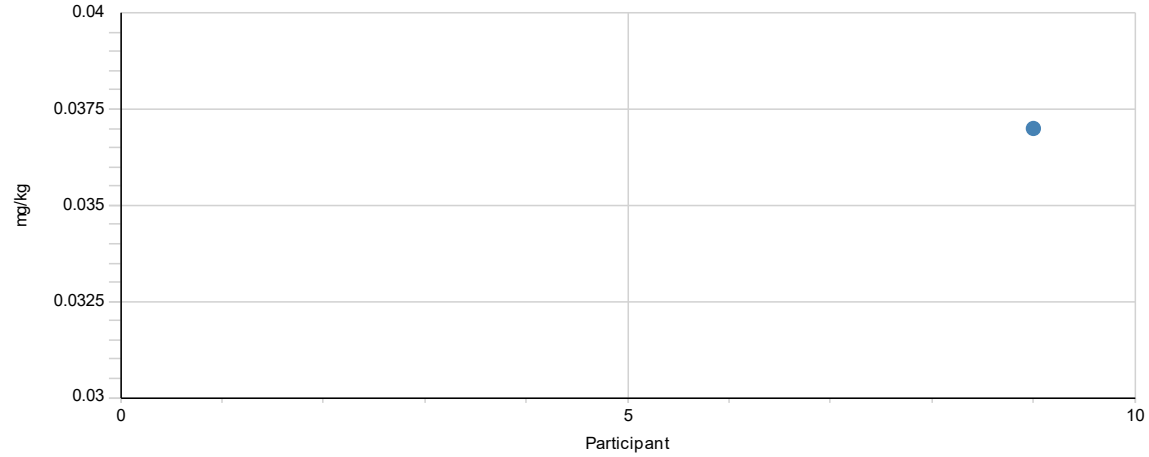
Measurand Ni Sample RT1LS10

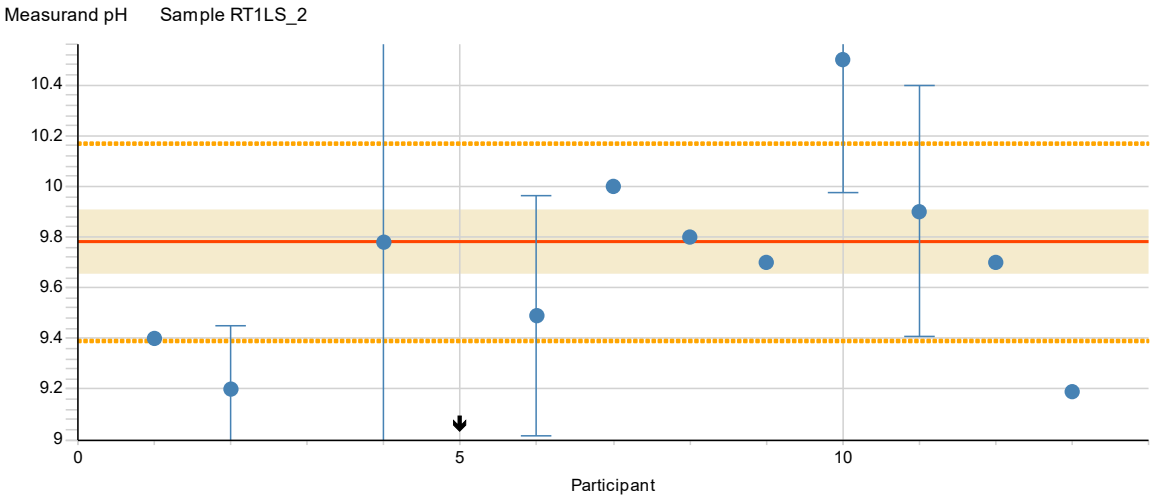


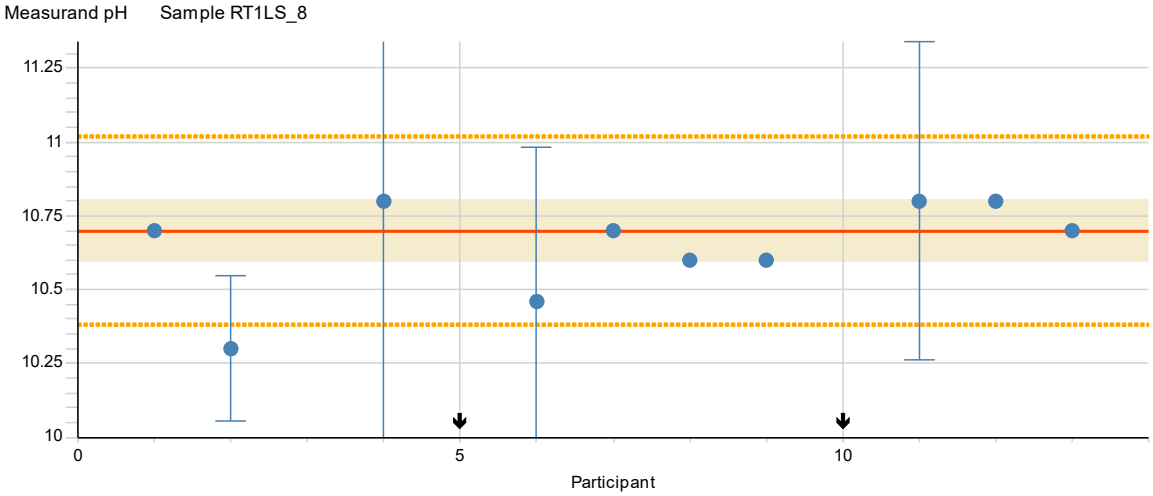
Measurand Pb Sample RT1LS_2

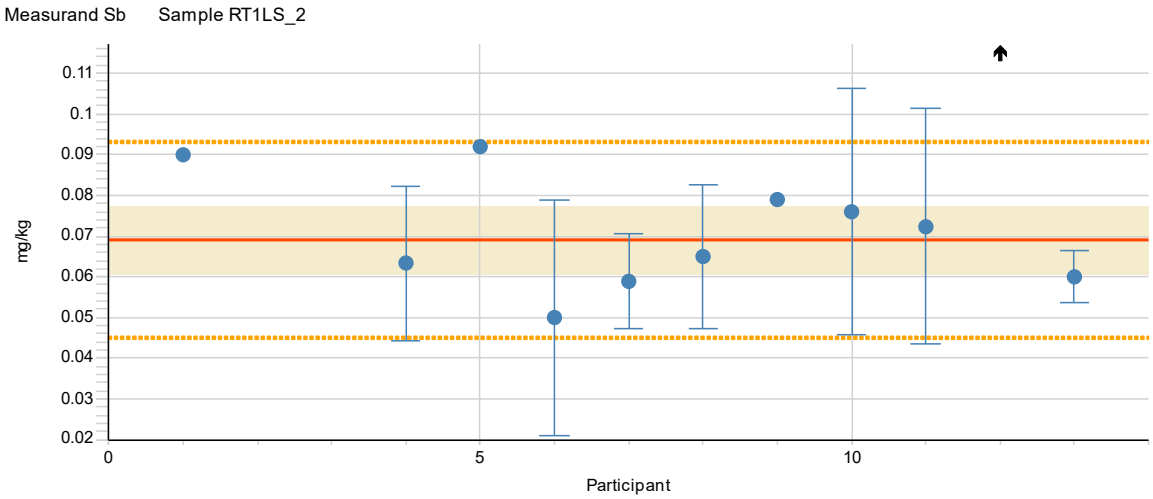


Measurand Pb Sample RT1LS10

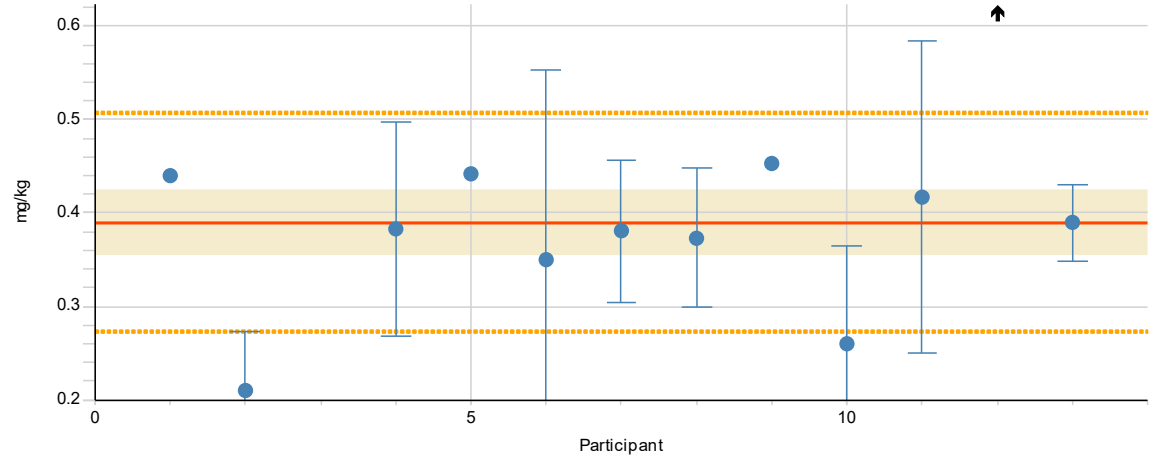



Measurand pH Sample RT1LS_2
10.4
10.2
10
9.8
9.6
9.4
9.2
9
0
5
10
Participant

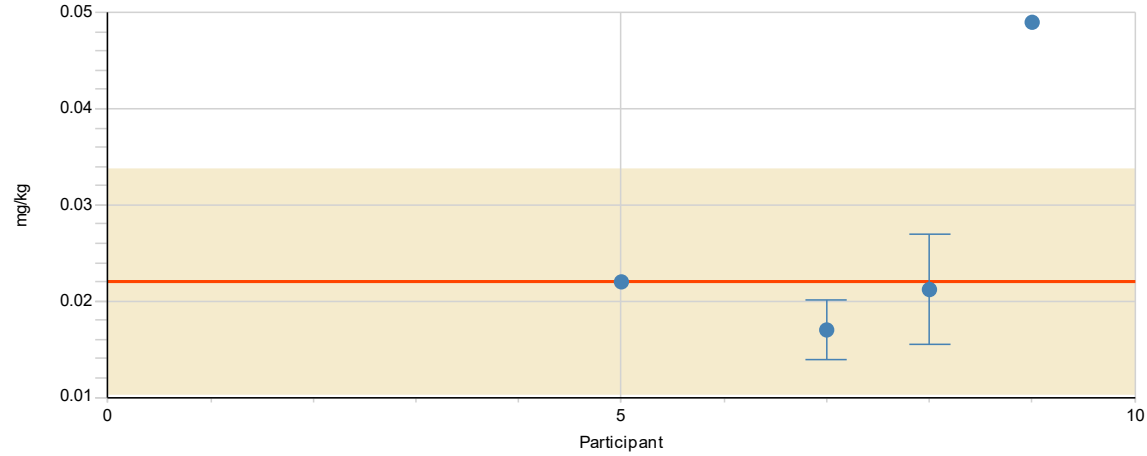

Measurand pH Sample RT1LS_8
11.25
11
10.75
10.5
10.25
10
0
5
10
Participant


Measurand Sb Sample RT1LS_2
mg/kg
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0
5
10
Participant

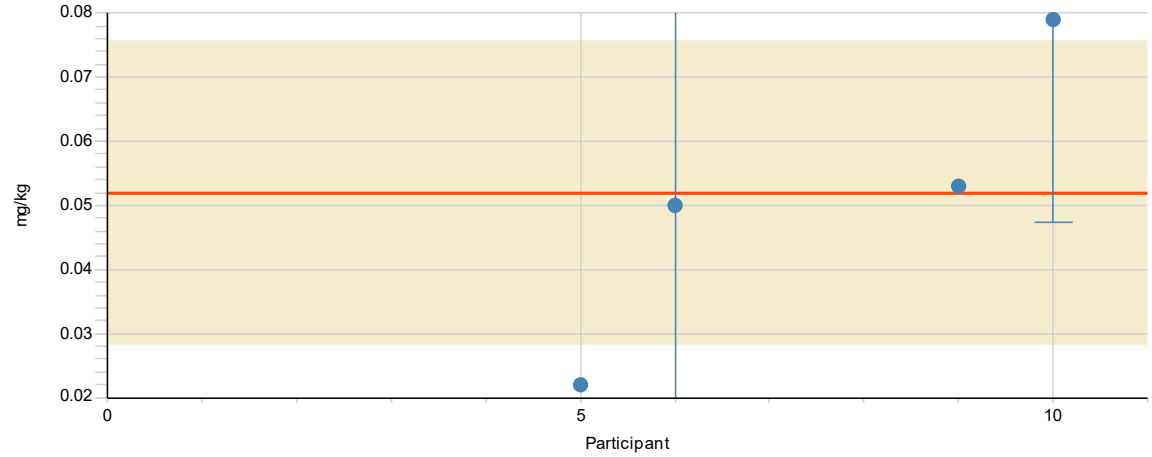
Measurand Sb Sample RT1LS10



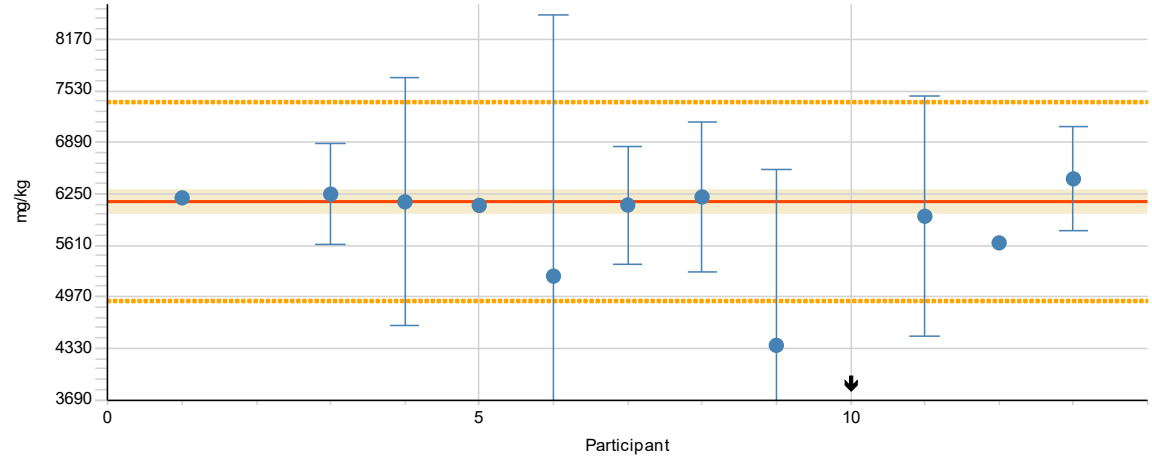
Measurand Se Sample RT1LS_2



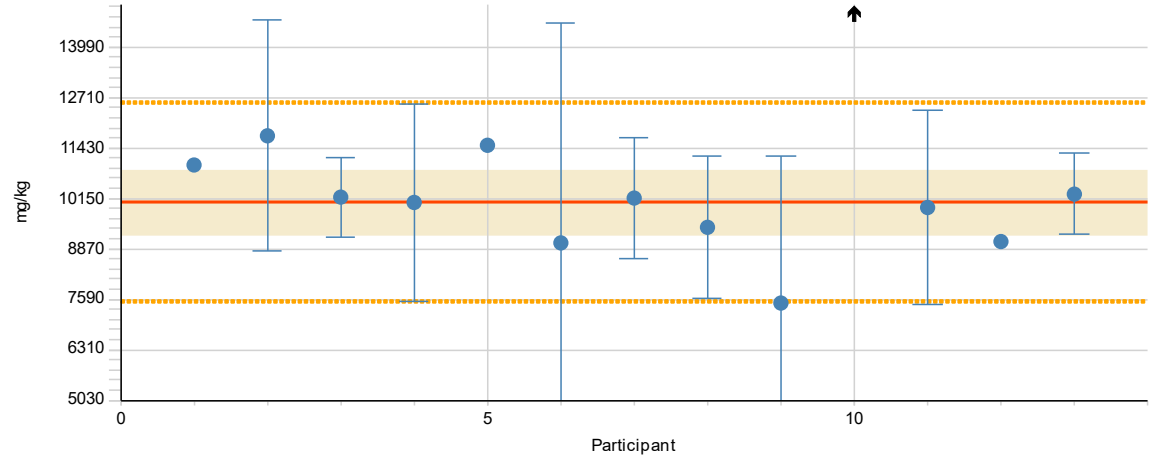
Measurand Se Sample RT1LS10



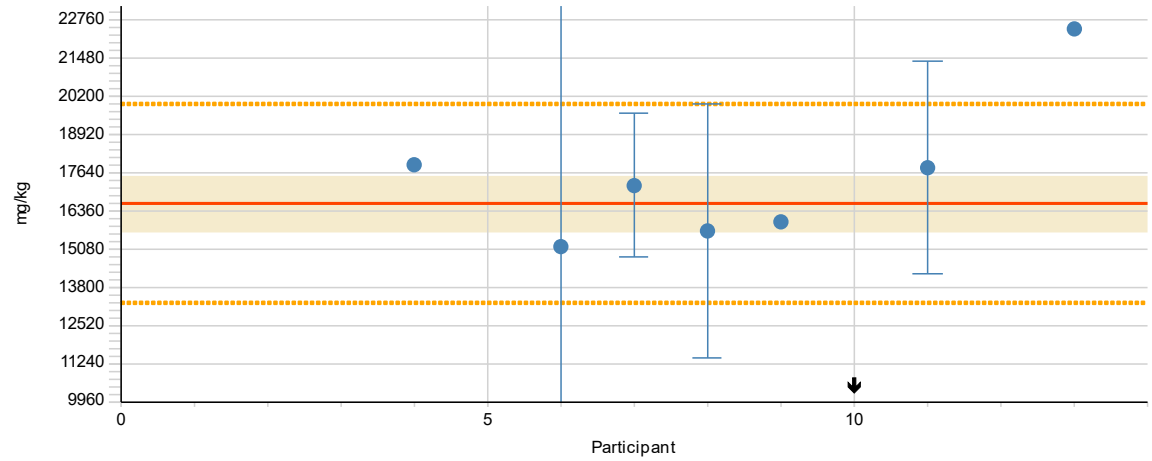
Measurand SO_4 Sample RT1LS_2



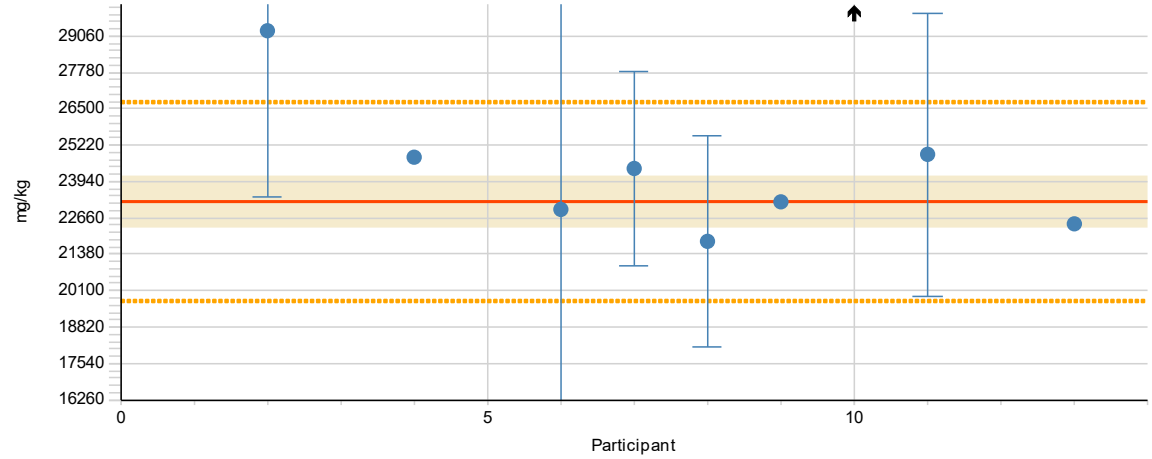
Measurand SO_4 Sample RT1LS10



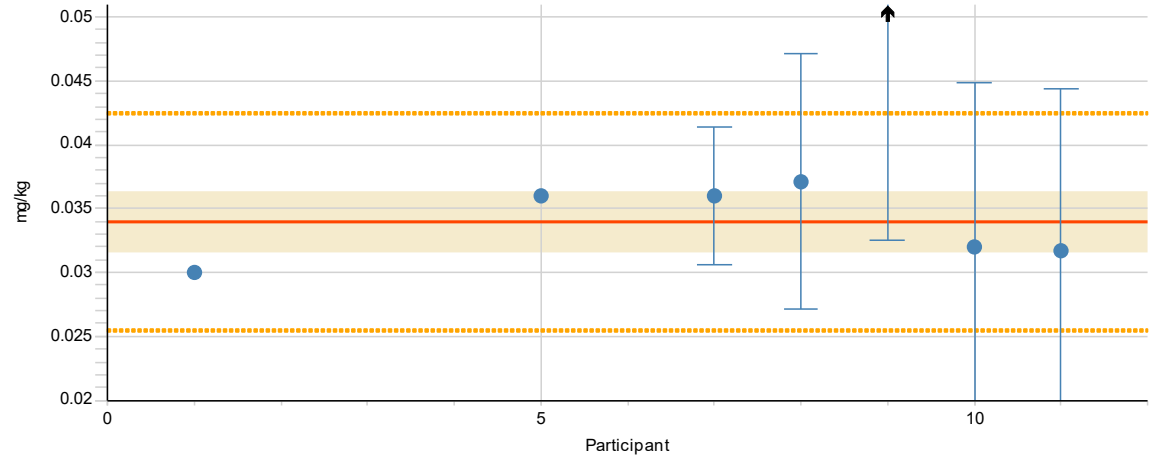
Measurand TDS Sample RT1LS_2



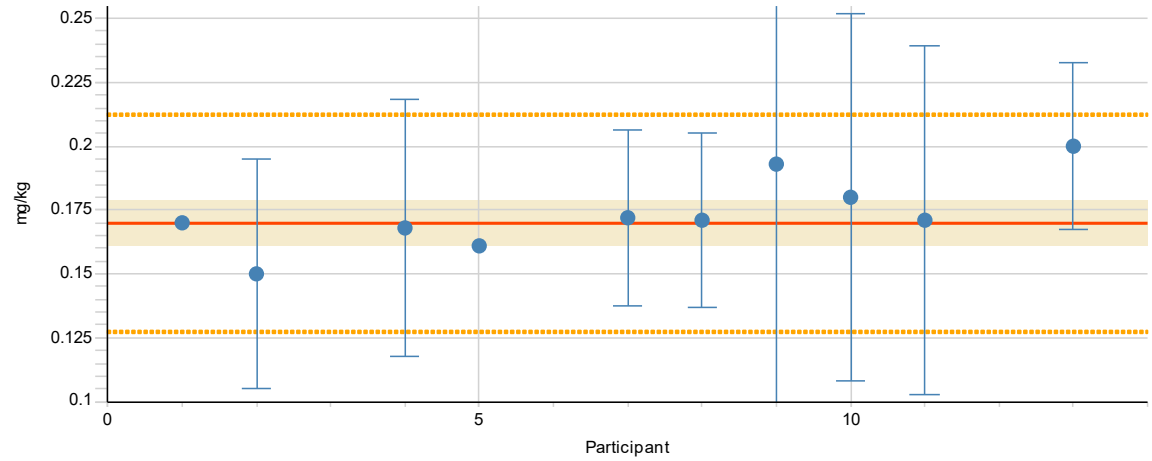
Measurand TDS Sample RT1LS10



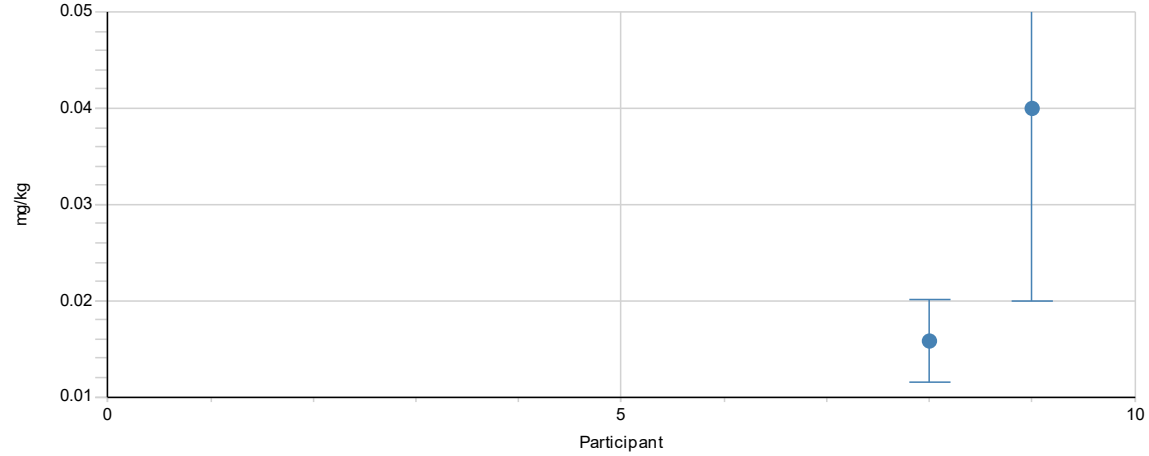
Measurand V Sample RT1LS_2



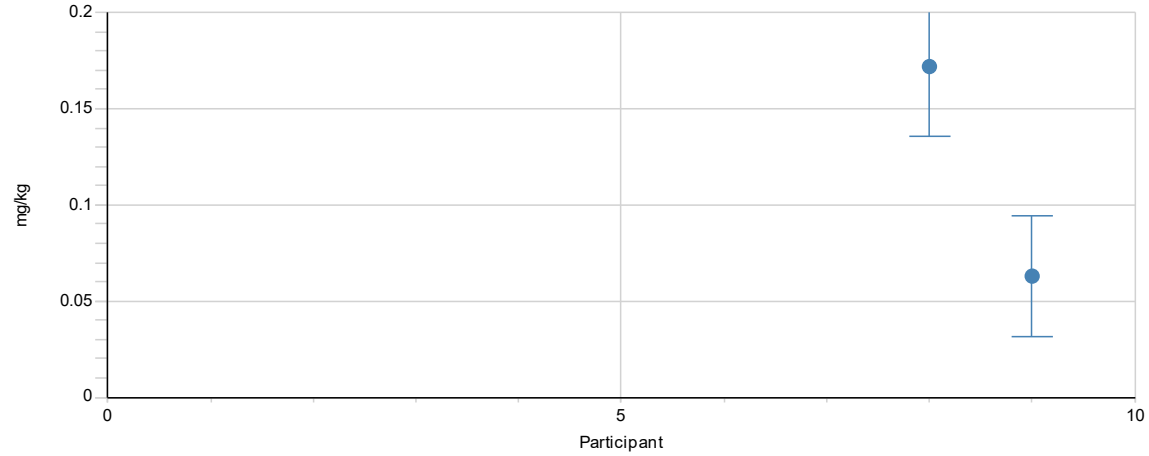
Measurand V Sample RT1LS10



Measurand Zn Sample RT1LS_2



Measurand Zn Sample RT1LS10



APPENDIX 8: Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	%
Ba	RT1LS10	*S*	*S*	.	**S**	*S*	.	**S**	**S**	U	**S**	**U**	.	**S**	80.0
Cl	RT1LS_2	S	.	.	**S**	*S*	**S**	**S**	**S**	S	**u**	**S**	*S*	**S**	90.9
	RT1LS10	*S*	**S**	.	**S**	*U*	**S**	**S**	**S**	S	**U**	**S**	*S*	**S**	83.3
Conductivity 25	RT1LS_2	.	*S*	.	**S**	.	**S**	**S**	**S**	S	**u**	**S**	*S*	*S*	90.0
	RT1LS_8	.	*U*	.	**S**	.	**S**	**S**	**S**	S	**U**	**S**	*S*	*S*	80.0
Cr	RT1LS_2	*S*	.	*S*	**S**	*S*	**S**	**S**	**S**	S	**u**	**S**	*S*	**Q**	83.3
	RT1LS10	*S*	*S*	*S*	**S**	*S*	**S**	**S**	**S**	S	**U**	**S**	*S*	**S**	92.3
Cu	RT1LS_2	*S*	.	*S*	**S**	*S*	.	**S**	**S**	S	**u**	**S**	.	**S**	90.0
	RT1LS10	*S*	*S*	*S*	**S**	*S*	**S**	**S**	**S**	S	**U**	**S**	.	**S**	91.7
DOC	RT1LS_2	.	.	.	**S**	.	**S**	**S**	**S**	S	*u*	**S**	.	*S*	87.5
	RT1LS10	.	**S**	.	**S**	.	**S**	**S**	**S**	S	*U*	**S**	.	*S*	88.9
Mo	RT1LS_2	*S*	.	*S*	**S**	*S*	**S**	**S**	**S**	S	**u**	**S**	*S*	**S**	91.7
	RT1LS10	*S*	*S*	*S*	**S**	*S*	**S**	**S**	**S**	S	**U**	**S**	*S*	**S**	92.3
pH	RT1LS_2	*S*	*q*	.	**S**	*u*	**S**	**S**	**S**	S	**U**	**S**	*S*	*u*	66.7
	RT1LS_8	*S*	*q*	.	**S**	*u*	**S**	**S**	**S**	S	**u**	**S**	*S*	*S*	75.0
Sb	RT1LS_2	*S*	.	.	**S**	*S*	**S**	**S**	**S**	S	**S**	**S**	*U*	**S**	90.9
	RT1LS10	*S*	*u*	.	**S**	*S*	**S**	**S**	**S**	S	**q**	**S**	*U*	**S**	75.0
SO_4	RT1LS_2	*S*	.	*S*	**S**	*S*	**S**	**S**	**S**	q	**u**	**S**	*S*	**S**	83.3
	RT1LS10	*S*	**S**	*S*	**S**	*S*	**S**	**S**	**S**	q	**U**	**S**	*S*	**S**	84.6
TDS	RT1LS_2	.	.	.	*S*	.	*S*	**S**	**S**	S	**u**	*S*	.	*U*	75.0
	RT1LS10	.	*U*	.	*S*	.	*S*	**S**	**S**	S	**U**	*S*	.	*S*	77.8
V	RT1LS_2	*S*	.	.	.	*S*	.	**S**	**S**	U	**S**	**S**	.	.	85.7
	RT1LS10	*S*	*S*	.	**S**	*S*	.	**S**	**S**	S	**S**	**S**	.	**S**	100
%		100	64	100	100	82	100	100	100	83	17	96	86	86	
accredited			3		20		17	23	23		21	21		14	

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 85 % in accredited: 87 % in non-accredited: 83

APPENDIX 9: Summary of the E_n scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13		%
As	RT1LS10	.	.	.	.	.	.	-0.8	-0.8	0.9	0.1	.	.	.	. . . . .	100
Ba	RT1LS_2	.	.	.	1.7	.	.	0.2	-0.2	0.5	-0.8	2.2	.	0.9	. . . . .	71.4
F	RT1LS10	.	1.1	.	.	.	.	.	0.3	.	.	.	.	.	. . . . .	50.0
Ni	RT1LS10	.	.	1.2	.	.	.	.	.	0.3	-0.5	.	.	.	. . . . .	66.7
Se	RT1LS_2	.	.	.	.	.	.	-0.4	-0.1	.	.	.	.	.	. . . . .	100
	RT1LS10	.	.	.	.	.	-0.1	.	.	.	0.7	.	.	.	. . . . .	100
%			0	0	0		100	100	100	100	100	0		100		

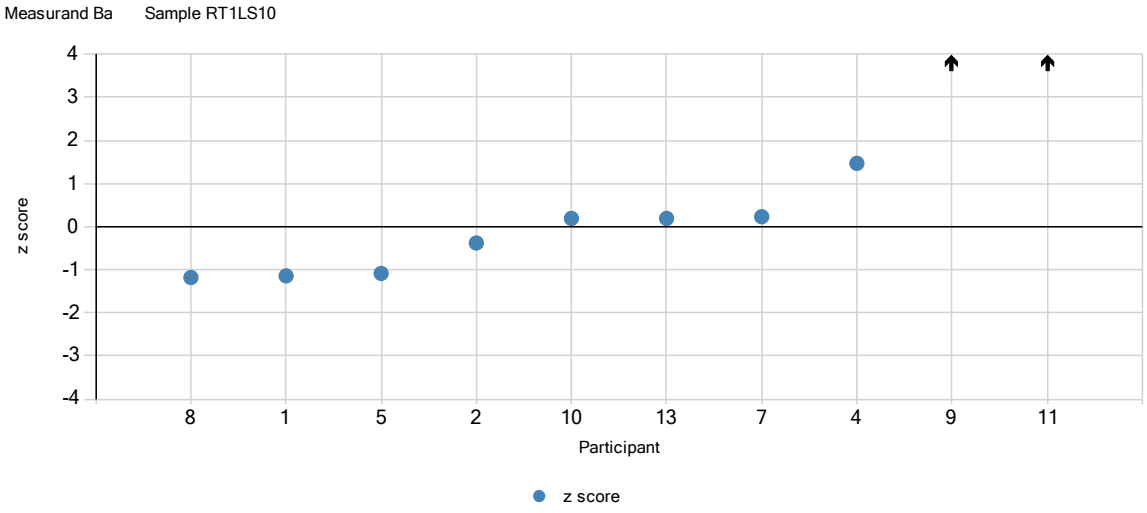
E_n scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty

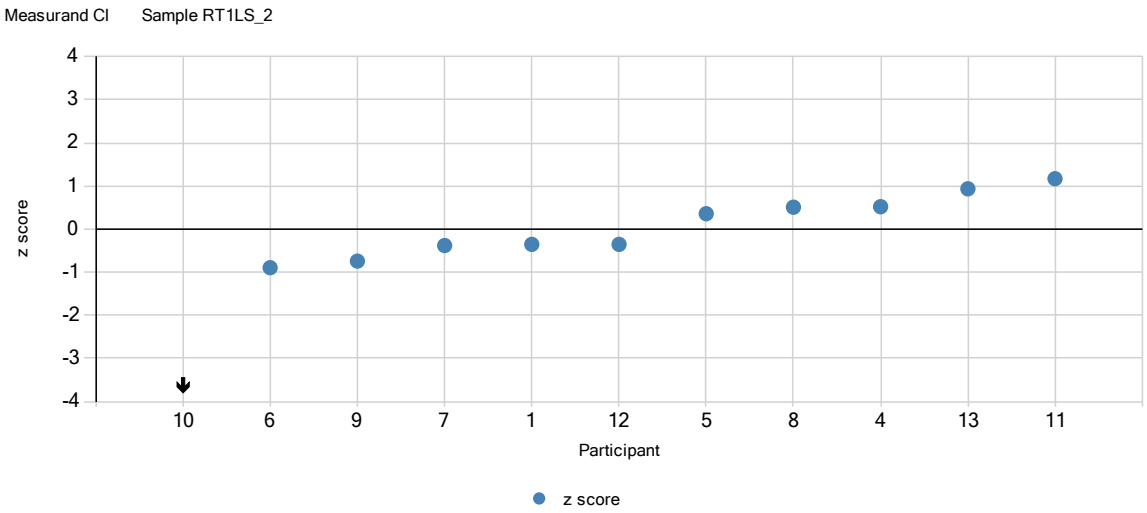
Scores of $-1.0 < E_n < 1.0$ indicate successful performance

Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

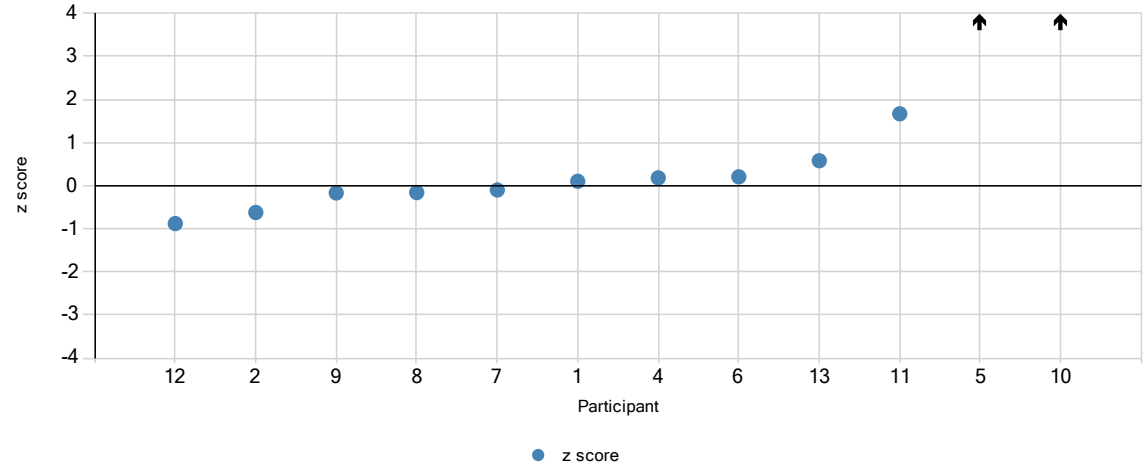
Totally satisfactory, % in all: 80

APPENDIX 10: z scores in ascending order

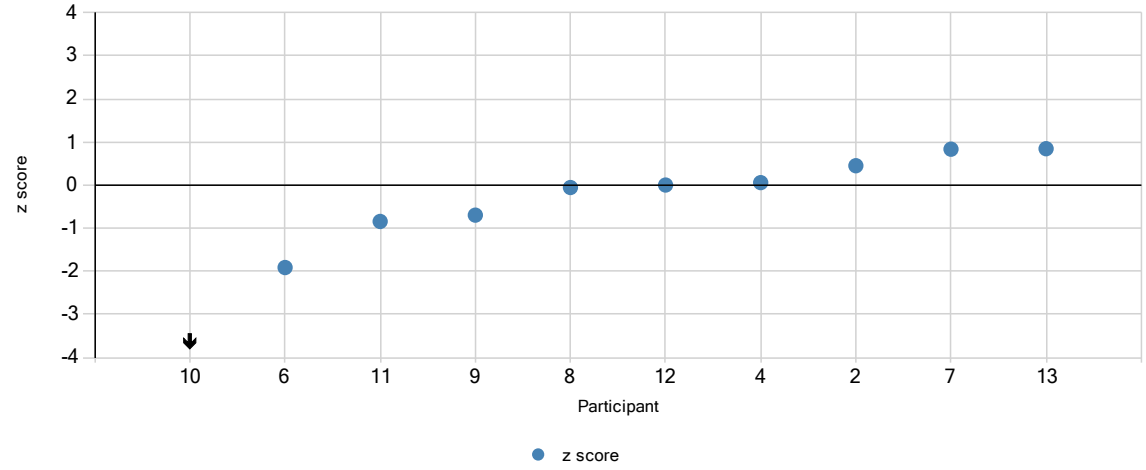




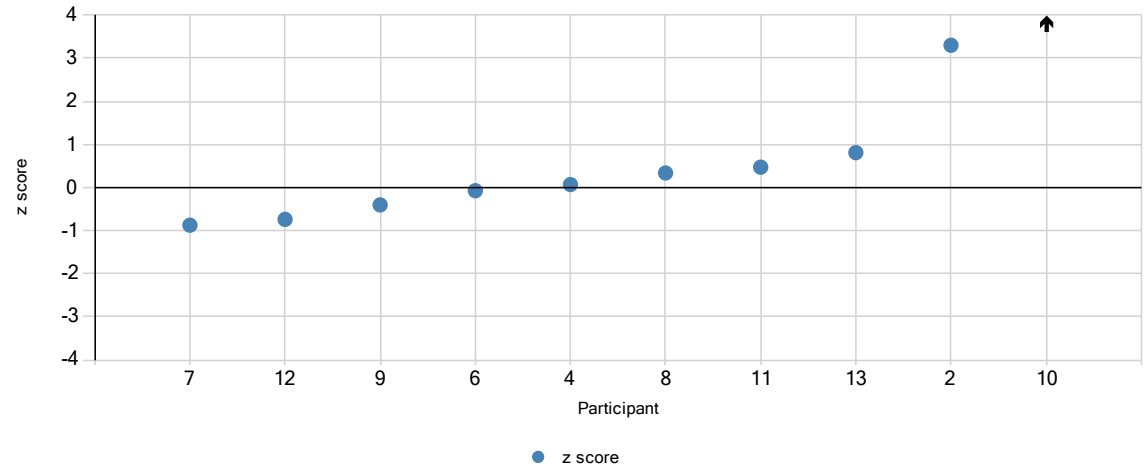
Measurand Cl Sample RT1LS10



Measurand Conductivity 25 Sample RT1LS_2



Measurand Conductivity 25 Sample RT1LS_8



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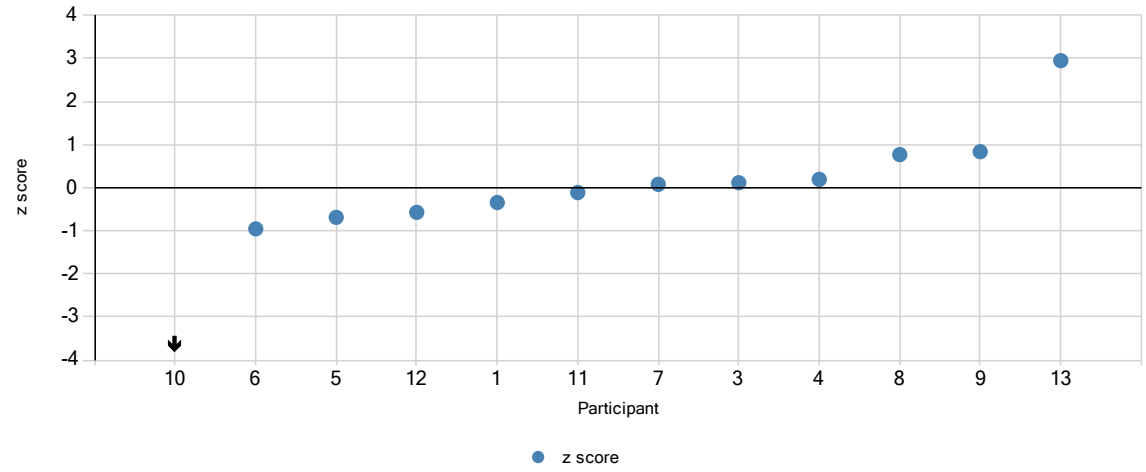
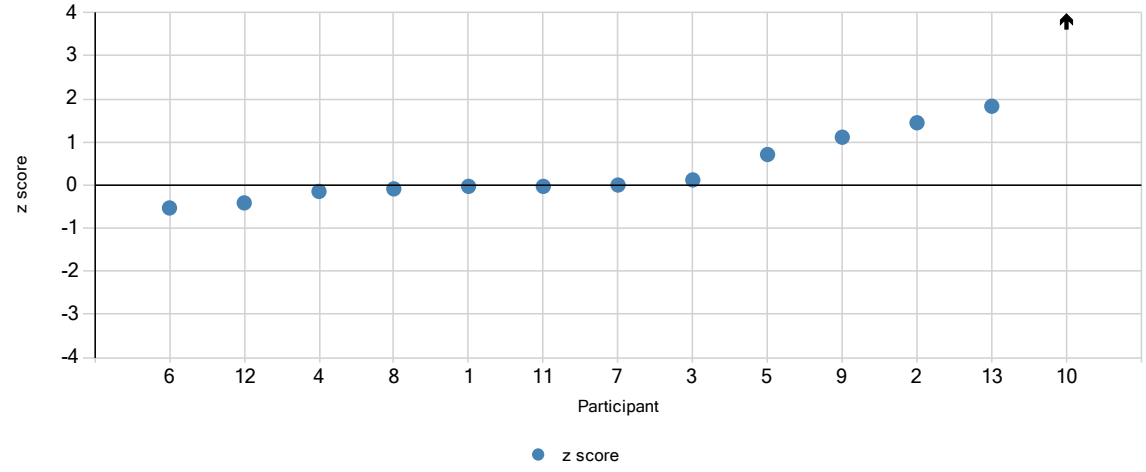
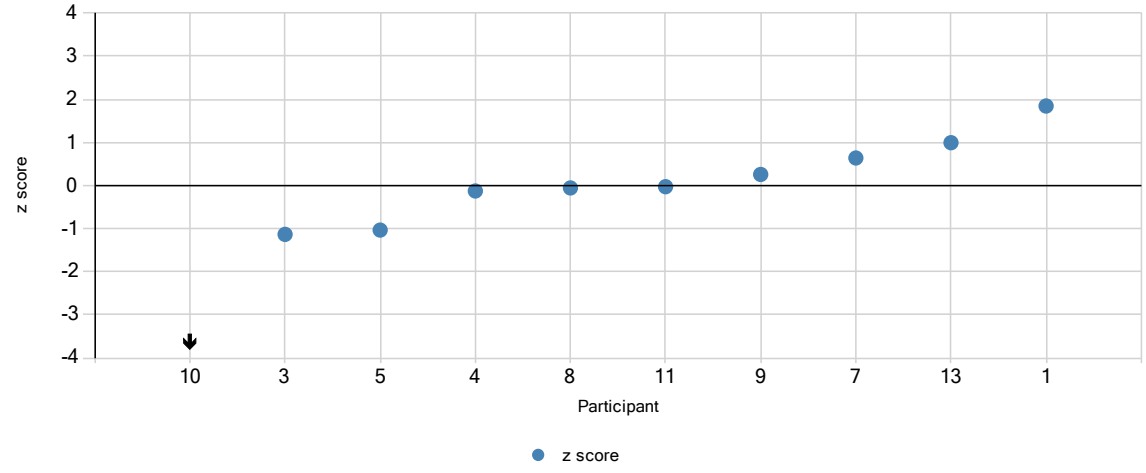


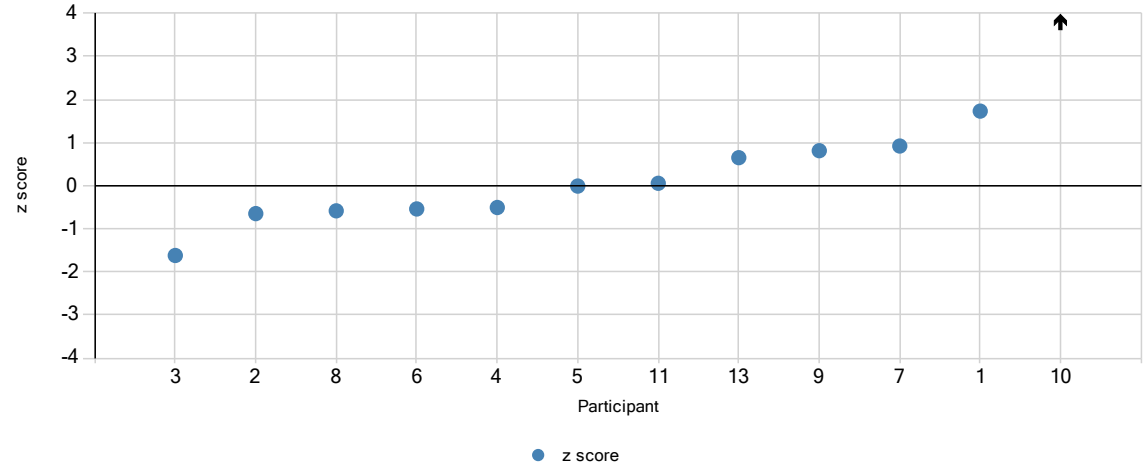
Measurand Cr Sample RT1LS10



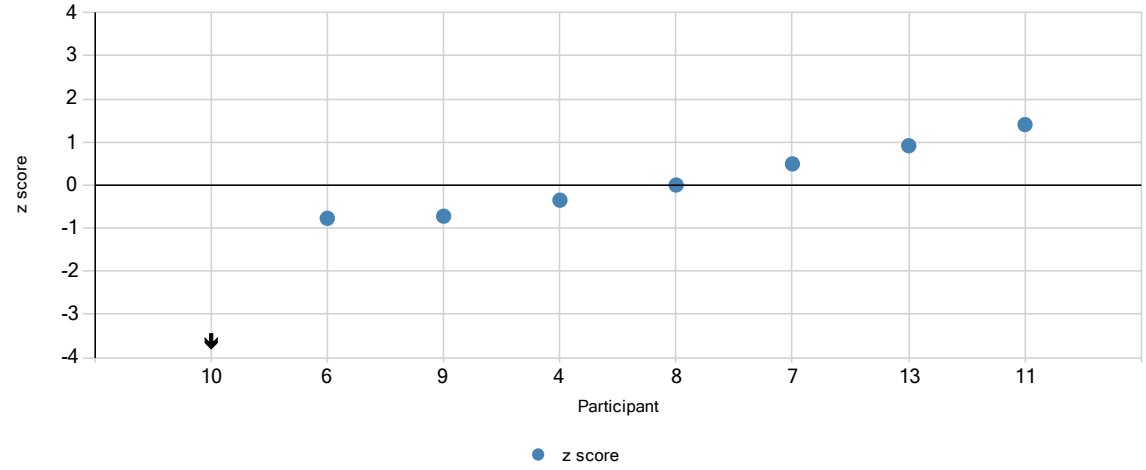
Measurand Cu Sample RT1LS_2



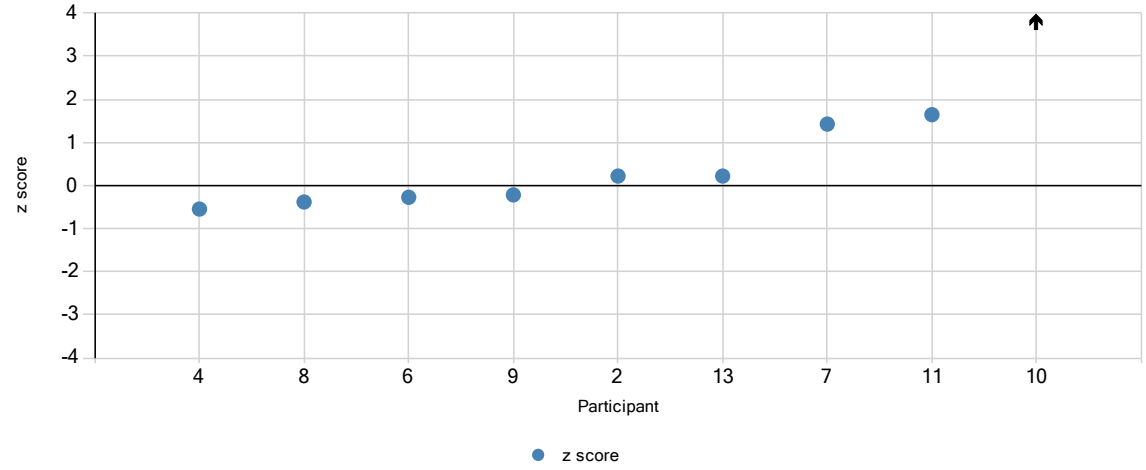
Measurand Cu Sample RT1LS10



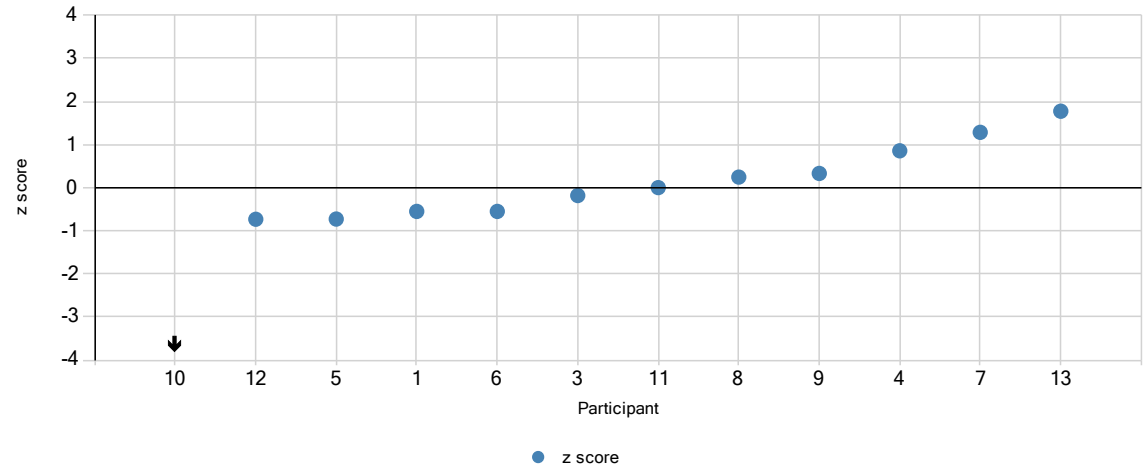
Measurand DOC Sample RT1LS_2



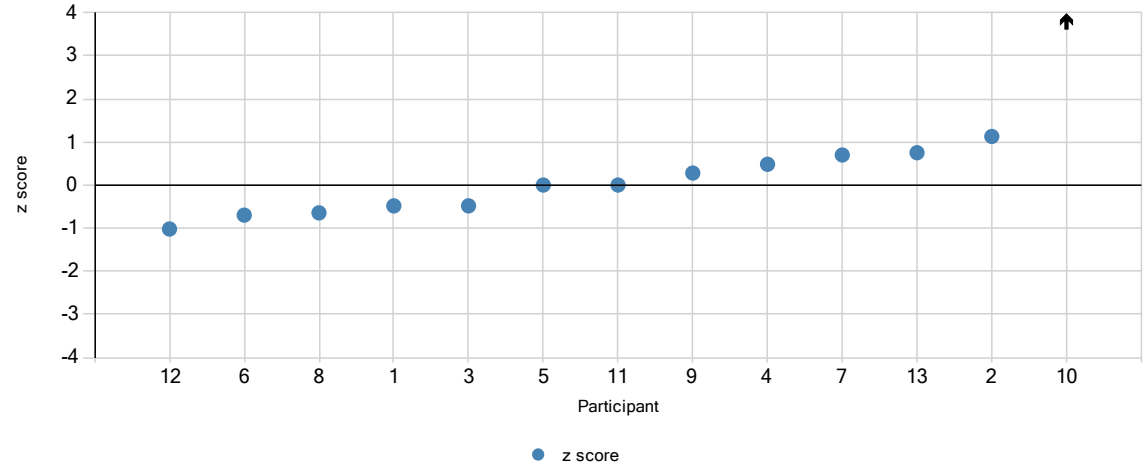
Measurand DOC Sample RT1LS10



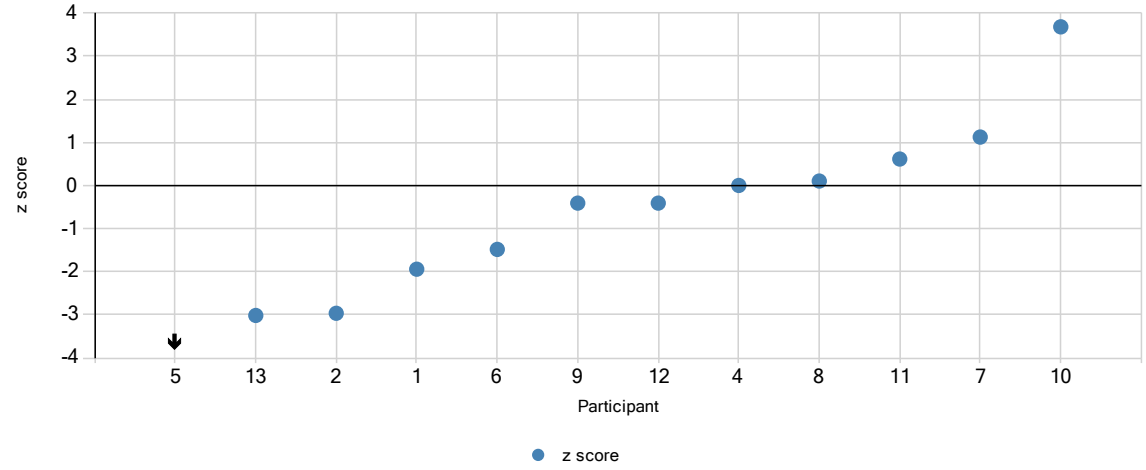
Measurand Mo Sample RT1LS_2



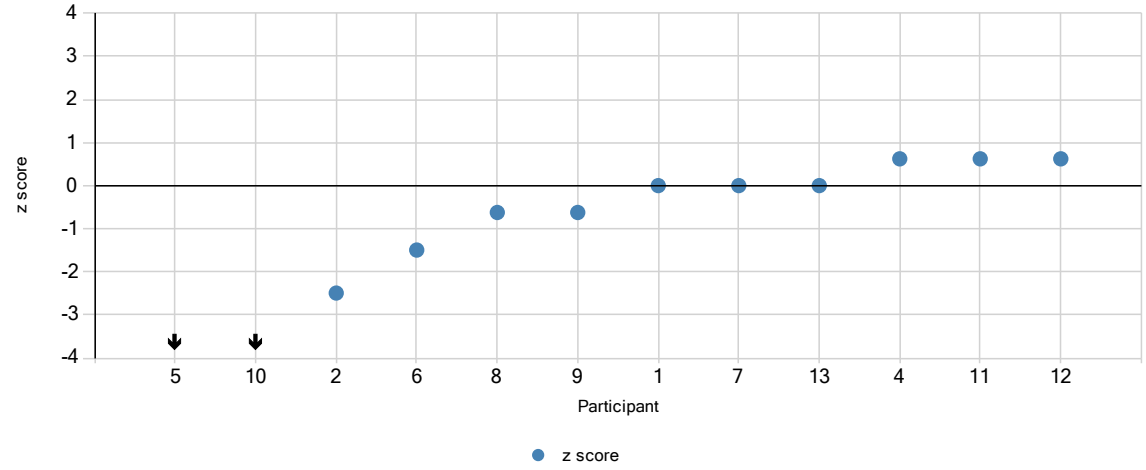
Measurand Mo Sample RT1LS10



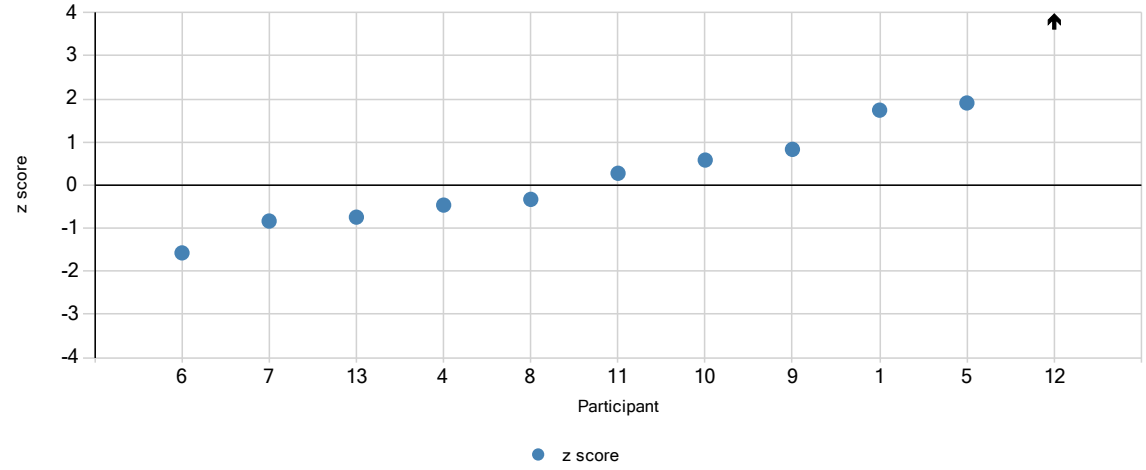
Measurand pH Sample RT1LS_2



Measurand pH Sample RT1LS_8



Measurand Sb Sample RT1LS_2



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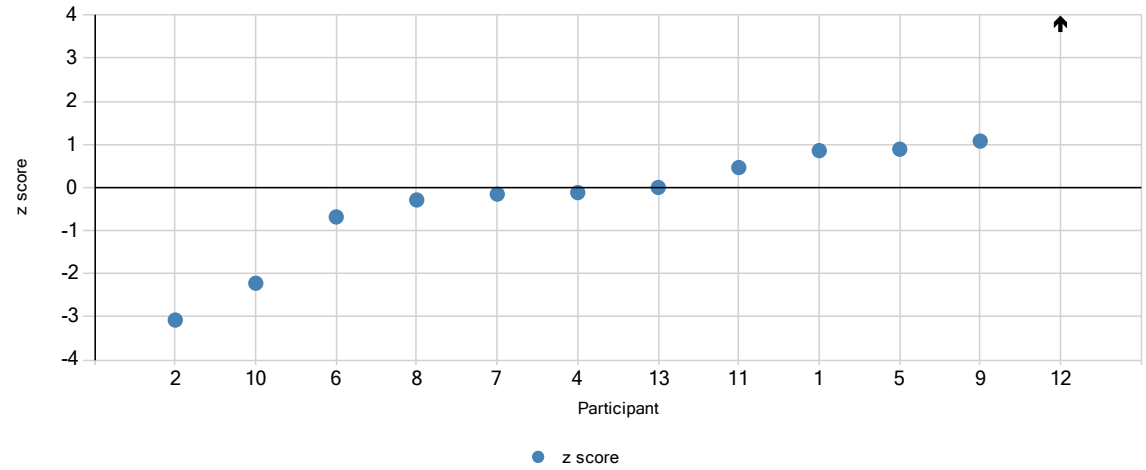
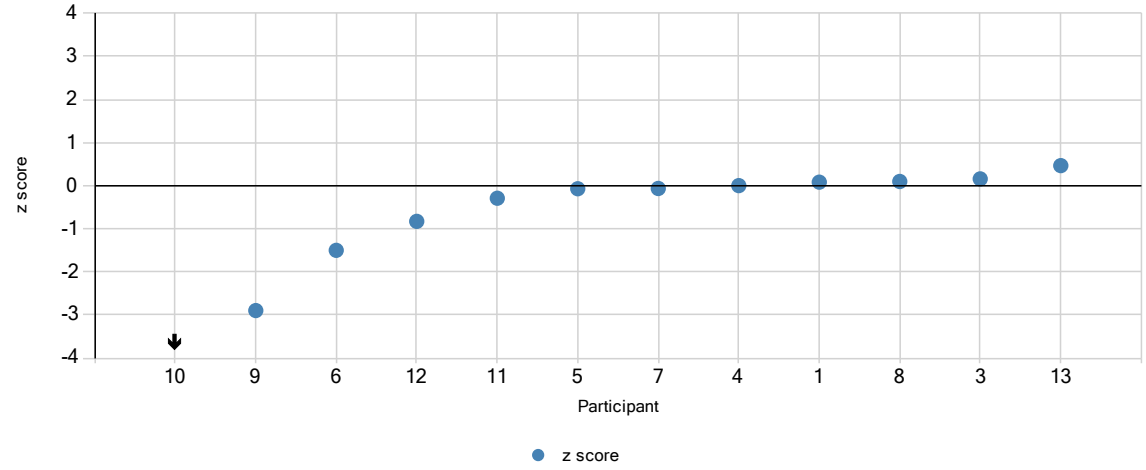
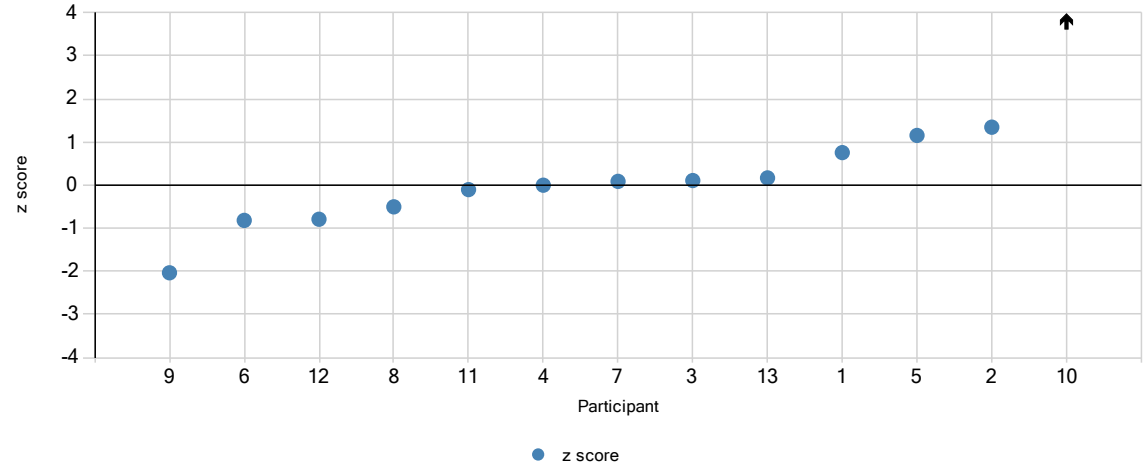


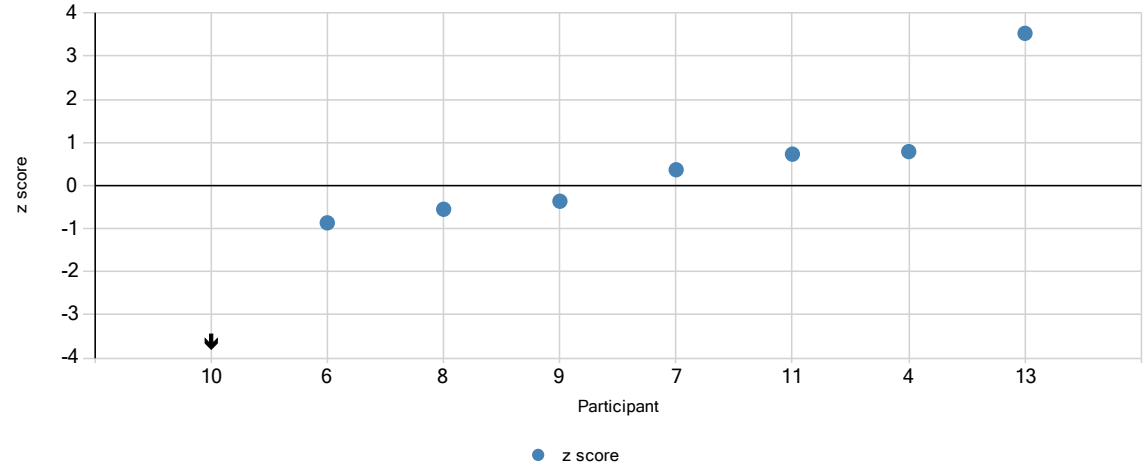
Measurand SO_4 Sample RT1LS_2



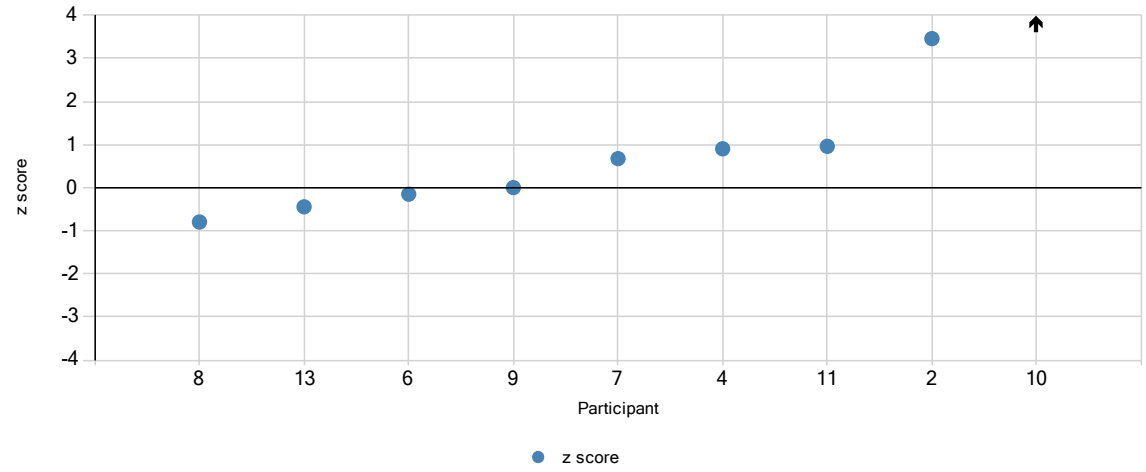
Measurand SO_4 Sample RT1LS10



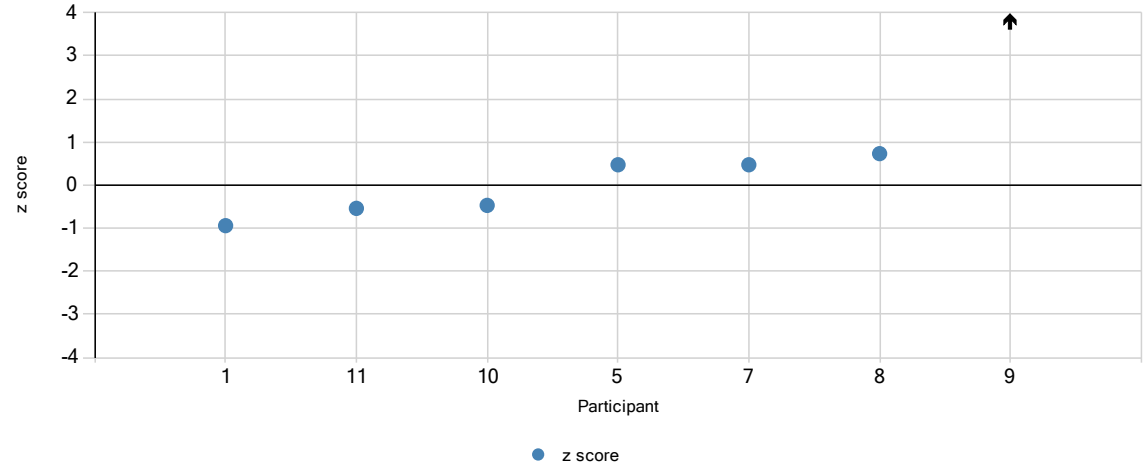
Measurand TDS Sample RT1LS_2



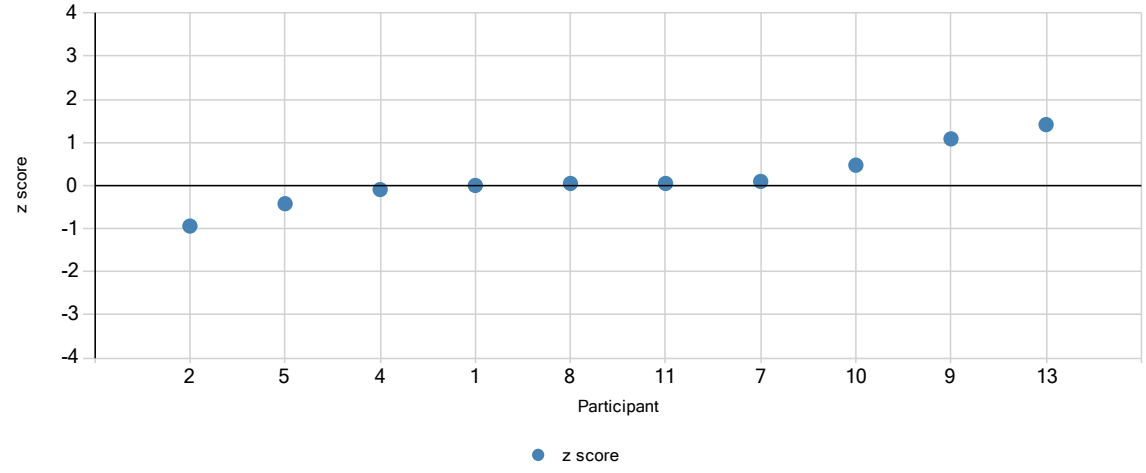
Measurand TDS Sample RT1LS10



Measurand V Sample RT1LS_2



Measurand V Sample RT1LS10



APPENDIX 11: Leaching test, production of eluate

Participant	Start date of the leaching test	Sample amount, Mw (kg)	Shaking/ mixing equipment [with rpm]	Description of the extraction: First and second leaching step [Bottle: type, size and material; duration (min)]	V of leachant, (l)	t(min) Agitation / separation, T1[1] and T3[2]	Description of the liquid-solid separation procedure (Separation method, type and material of the filter, pore size)	Centrifugation	t(min) Filtration, T2[3] and T4[4]	V of filtered eluate, VE1[5] and VE2[6] (l)
1	11.05.2020	0.104	Heidolph Reax 20 [~8 rpm]	**L_2:** 1000ml glass bottle, 360 min +/- 30 min **L_8:** 1000ml glass bottle, 1080min	**L_2:** 0.196 **L_8:** 0.8	**T1:** 15 **T3:** 15	**L_2 and L_8:** Vacuum filtration, 0.45µm MCE membrane filter and vacuum filtering equipment	–	**T2:** 37 **T4:** 60	**VE1:** 0.156 **VE2:** 0.790
4	5.5.2020	175	End-over [10 rpm]		**L_2:** 0.342 **L_8:** 1400	**T3:** 15	**L_2 and L_8:** Gelman 0.45 µm	–	**T2:** 20 **T4:** 20	**VE1:** 0.250
5	23.4.2020	0.200	[8 rpm]	**L_2:** Plastic bottle (PET), 1 liter, 24 h **L_8:** Syringe, 6 ml, natural rubber latex, 0.5 min	**L_2:** 1 **L_8:** 0.005	**T1:** 30 **T3:** 1	**L_2:** vacuum pump, membrane filter, 0.45 micron **L_8:** separation with FLL / MLL filter Acrylic, 0.45 micron	–	**T2:** 60 **T4:** 1	**VE1:** 1 **VE2:** 0.005
6	11.5.2020	0.1	Heidolph Reax 20 [5-10 rpm]	**L_2:** 1 l glass bottle, duration 5h 57 min **L_8:** 1 l glass bottle, duration 17h 48 min	**L_2:** 0.196 **L_8:** 0.8	**T1:** 10 **T3:** 10	**L_2 and L_8:** High pressure filtration equipment 5 bar, 0.45µm membrane filter Whatman NC45, cellulose-nitrate membrane filter, diameter 142 mm	–	**T2:** 2 **T4:** 1	**VE1:** 0.150 **VE2:** 0.3
7	19.5.2020	0.183	Turn-over head shaker, [10 rpm]	**L_2:** PE 0.5 l, 6 h **L_8:** PE 2 l, 18 h	**L_2:** 0.342 **L_8:** 1.4	**T1:** 20 **T3:** 15	**L_2 and L_8:** Vacuum filtration, <0.45 µm membrane	–	**T2:** 25 **T4:** 25	**VE1:** 0.30 **VE2:** 1.35
8	5.5.2020	0.1818	Rotary shaker [8 rpm]	**L_2:** plastic, polypropylene 500ml, 360 min **L_8:** plastic, polypropylene 2000ml, 1080 min	**L_2:** 0.343 **L_8:** 1.4	**T1:** 15 **T3:** 15	**L_2 and L_8:** pressure filtration - membrane filter - pore size: 0.4um	**L_2 and L_8:** 8 min, 4500 rpm	**T2:** 20 **T4:** 30	**VE1:** 235 **VE2:** 0.4
9	19.5.2020	0.175	Heidolph Reax 20 [2 rpm]	**L_2:** Glass bottles with cap, 500 ml, 360min **L_8:** Glass bottles with cap, 2 l, 1080min	**L_2:** 0.344 **L_8:** 1.4	**T1:** 15 **T3:** 15	**L_2 and L_8:** Pressure filtration, Whatman Grade 934AH Glass fiber filters, 47mm	**L_2 and L_8:** 5 min, 4000 rpm	**T2:** 55 **T4:** 50	**VE1:** 200 **VE2:** 1.3
12	4.5.2020	0.175	Heidoplh Reax 20 [7 rpm]	**L_2:** 500 ml HDPE square bottle, duration 360 min **L_8:** 2000 ml HDPE square bottle, duration 1080 min	**L_2:** 0.35 **L_8:** 1.4	**T1:** 1 **T3:** 15	**L_2:** Suction bottle filtration, Whatman 0903, cellulose, permeability 4.7µm **L_8:** Centrifugation, filtration with syringe filter 0.45 µm	**L_2:** No **L_8:** 10 min, 7000 rpm	**T2:** 10	**VE1:** 0.265
13	4.5.2020	0.183	Edmund Bühler 30C Control [10 rpm]	**L_2:** Plastic bottle, 500 ml and HDPE; 360 min **L_8:** Plastic bottle, 2000 ml and HDPE; 1080 min	**L_2:** 0.342 **L_8:** 1.4	**T1:** 15 **T3:** 10	**L_2 and L_8:** Vacuum filtration, Whatman membrane filter, "mixed cellulose ester", pore size 0.45 µm	–	**T2:** 60	**VE1:** 0.238

[1] T1 = Settling time between first agitation and separation

[2] T3 = Settling time between second agitation and separation

[3] T2 = Duration of the first filtration

[4] T4 = Duration of the second filtration

[5] VE1 = Volume of the first eluate

[6] VE2 = Volume of the second eluate

APPENDIX 12: Method of analysis by measurands

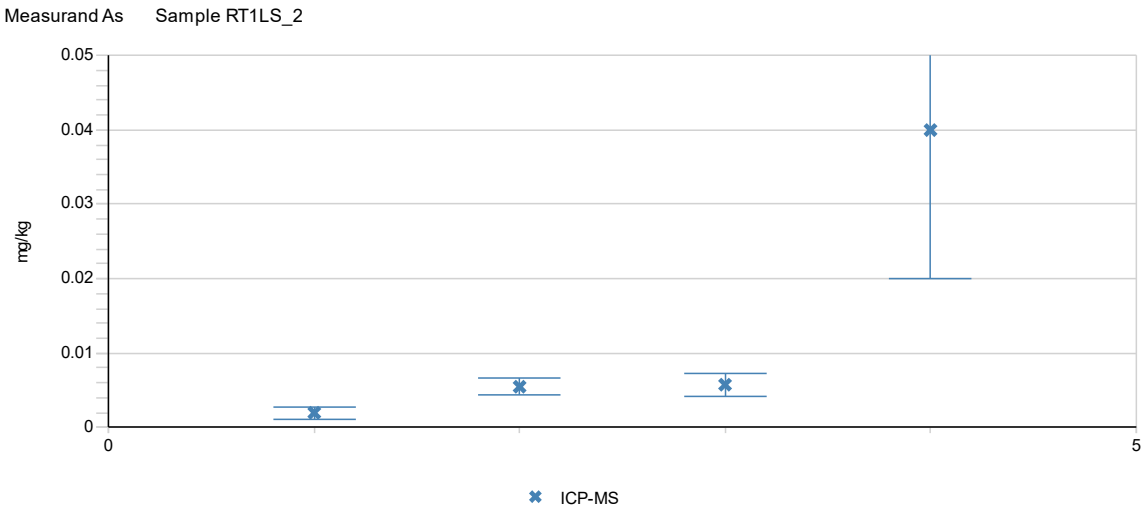
Measurand	Standard options	No. of participants	Applied / modified / more information	No. of participants
As n=9 (the number of participants who answered)	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Ba n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Cd n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Cl^- n=8	EN ISO 10304-1:2009	6	Internal method, based on this standard	5
			Modified	1
	Other method	2	Modified: ICP-OES	1
			Modified: Cuvette test	1
Conductivity n=7	EN 27888:1993	7	Internal method, based on this standard	5
			Modified	2
Cr n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1

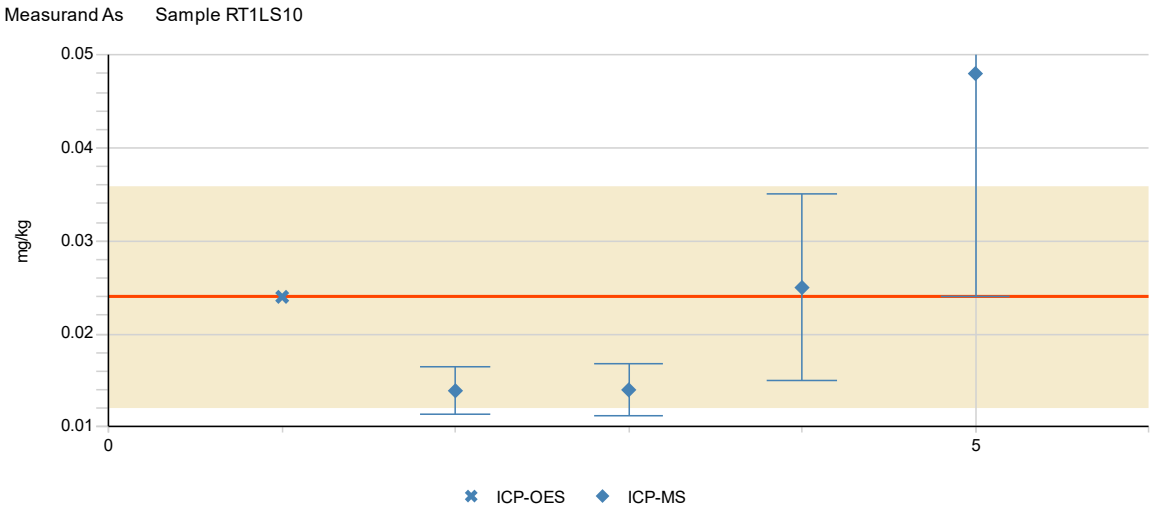
Measurand	Standard options	No. of participants	Applied / modified / more information	No. of participants
Cu n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
DOC n=5	EN 1484:1997	5	Internal method, based on this standard	5
F^- n=7	EN ISO 10304-1:2009	6	Internal method, based on this standard	5
			Modified	1
	Other method	1	Modified: Measurement with ion selective electrode	1
Hg n=9	EN 1483:2007	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17852:2008	3	Internal method, based on this standard	3
	Other method	4	Internal method, based on standard: EN ISO 17294-2:2004	1
			Internal method, based on standard: EN ISO 17294-2:2016	1
			Modified: EN ISO 17294-1:2006	1
			Modified: ICP-OES	1
Mo n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Ni n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Pb n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1

Measurand	Standard options	No. of participants	Applied / modified / more information	No. of participants
pH n=9	ISO 10523:2008	7	Internal method, based on this standard	5
			Modified	2
	Other	2	Modified: SFS 3021	1
			Modified: Internal method	1
Sb n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Se n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
SO_4^{2-} n=8	EN ISO 10304-1:2009	6	Internal method, based on this standard	5
			Modified	1
	Other method	2	Modified: ICP-OES	2
TDS n=5	EN 15216:2007	4	Internal method, based on this standard	4
	Other method	1	Internal method, based on standard: EN 15216:2008	1
V n=9	EN ISO 11885:2009	2	Internal method, based on this standard	1
			Modified	1
	EN ISO 17294-1:2006	3	Internal method, based on this standard	2
			Modified	1
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1
Zn n=9	EN ISO 11885:2009	3	Internal method, based on this standard	1
			Modified	2
	EN ISO 17294-1:2006	2	Internal method, based on this standard	2
	EN ISO 17294-2:2004	2	Internal method, based on this standard	2
	Other method	3	Internal method, based on standard: EN ISO 17294-2:2016	2
			Modified: ICP-OES	1

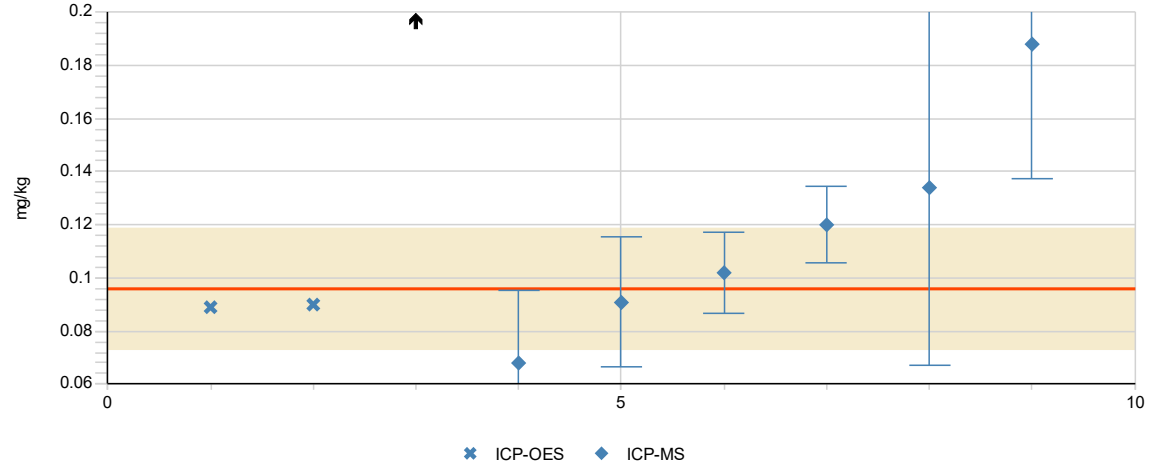
APPENDIX 13: Results grouped according to the methods

The explanations for the figures are described in the Appendix 7. The results are shown in ascending order.





Measurand Ba Sample RT1LS_2



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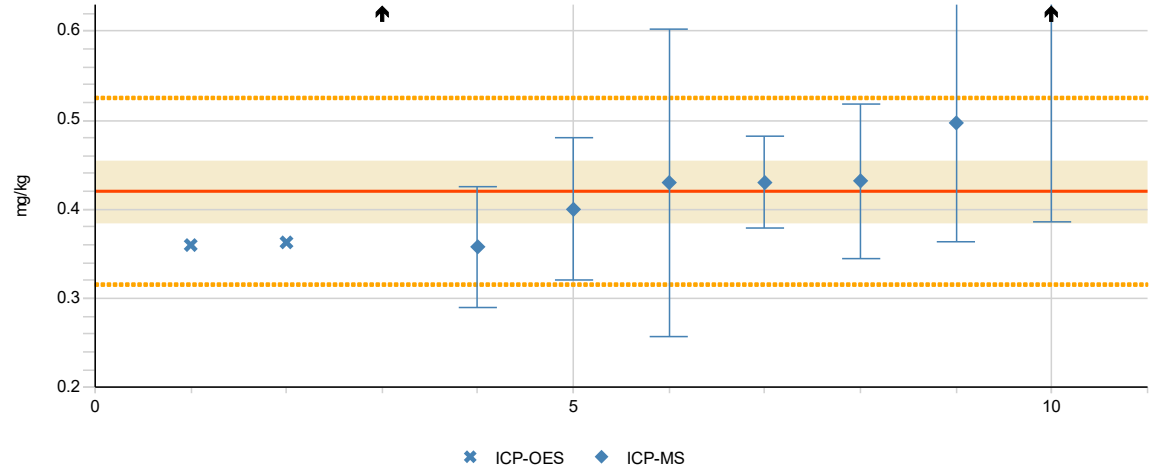
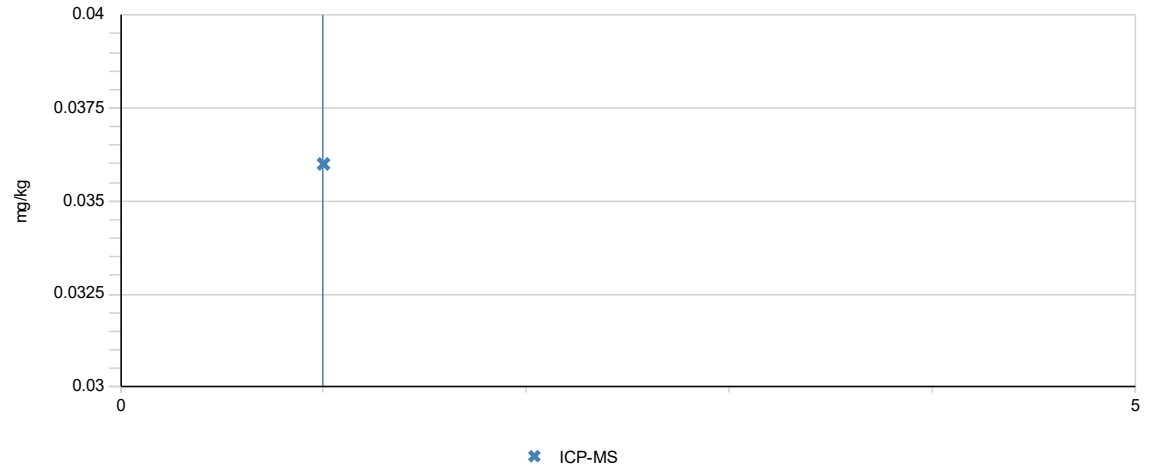


Measurand Cd Sample RT1LS_2



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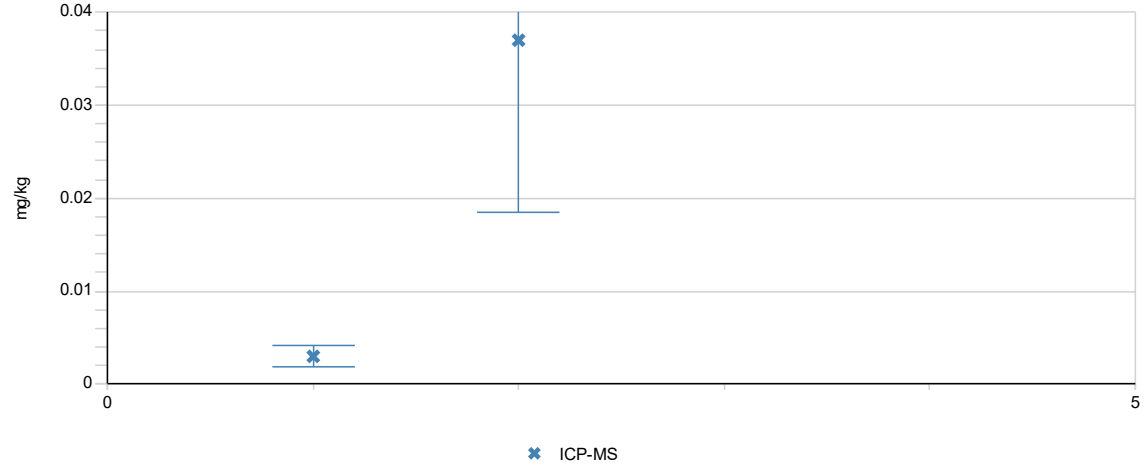

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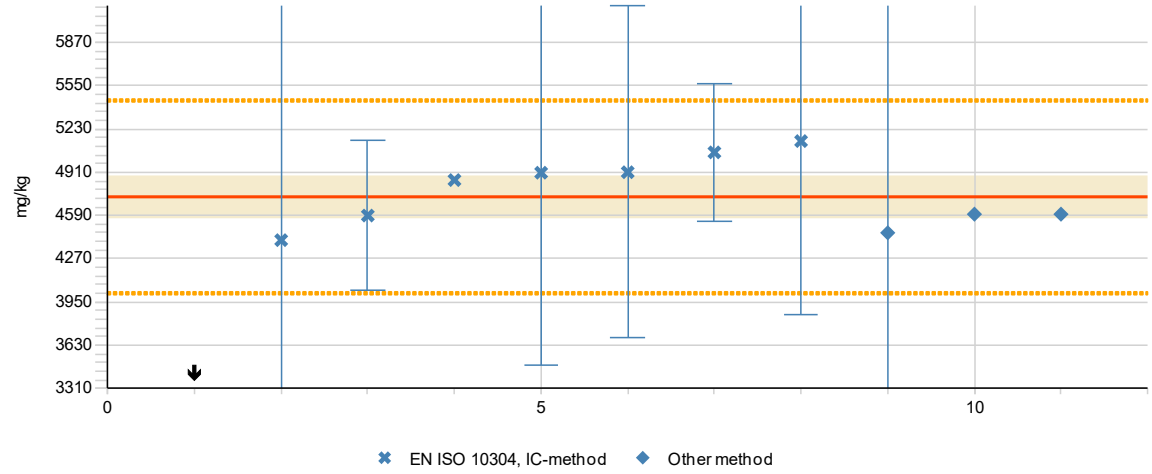
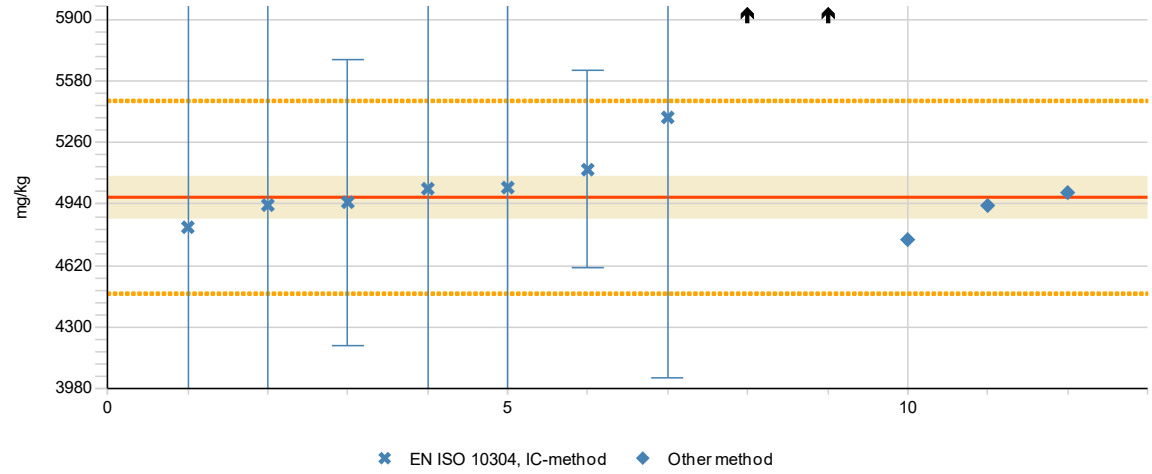
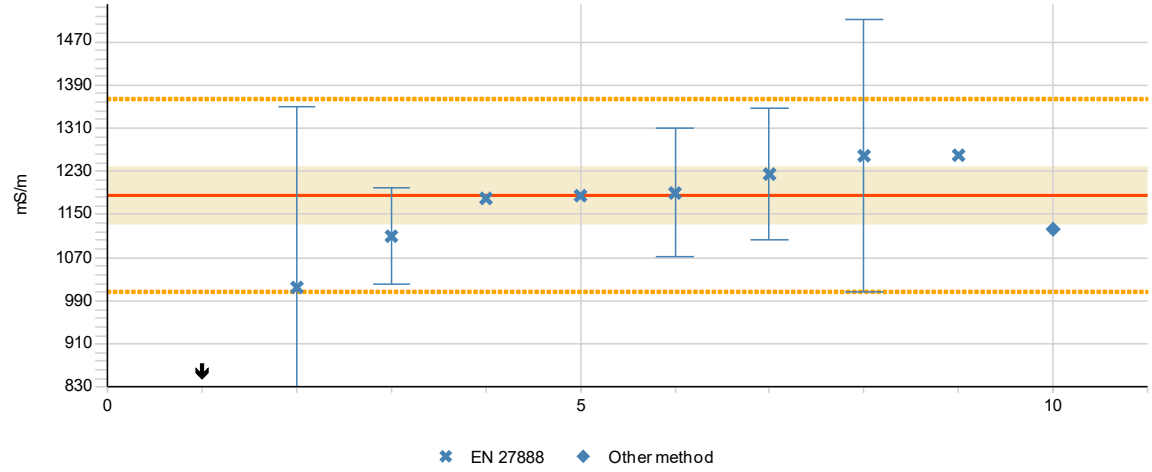


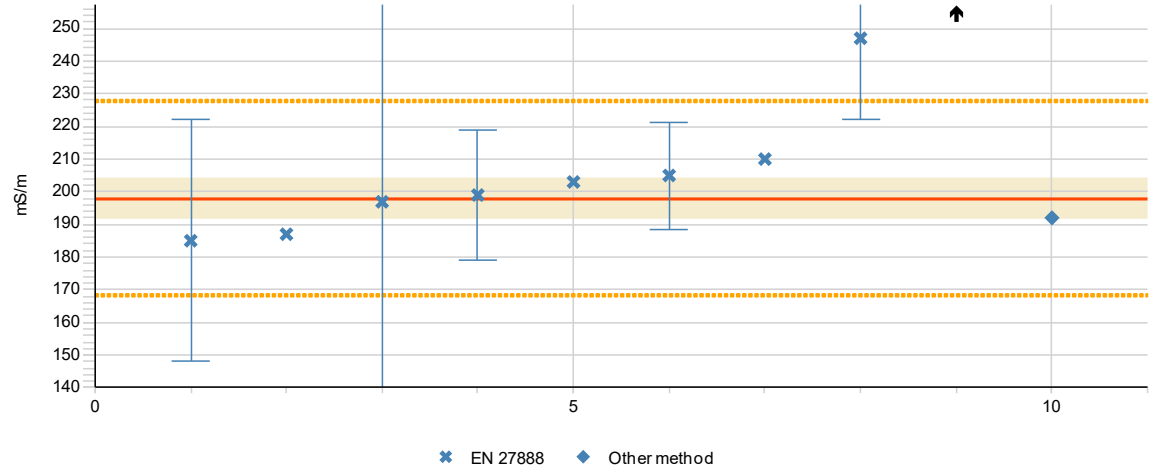
Measurand Cl Sample RT1LS10



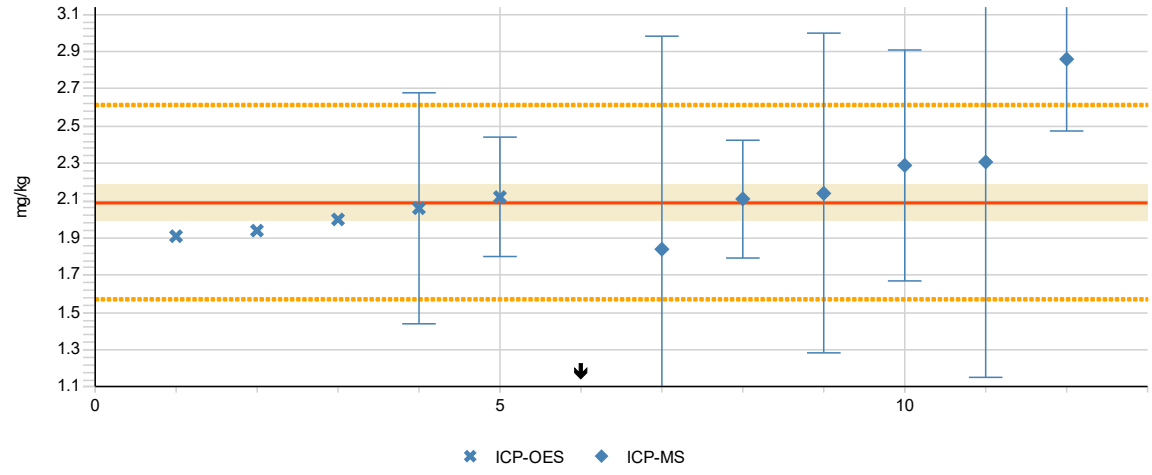
Measurand Conductivity 25 Sample RT1LS_2



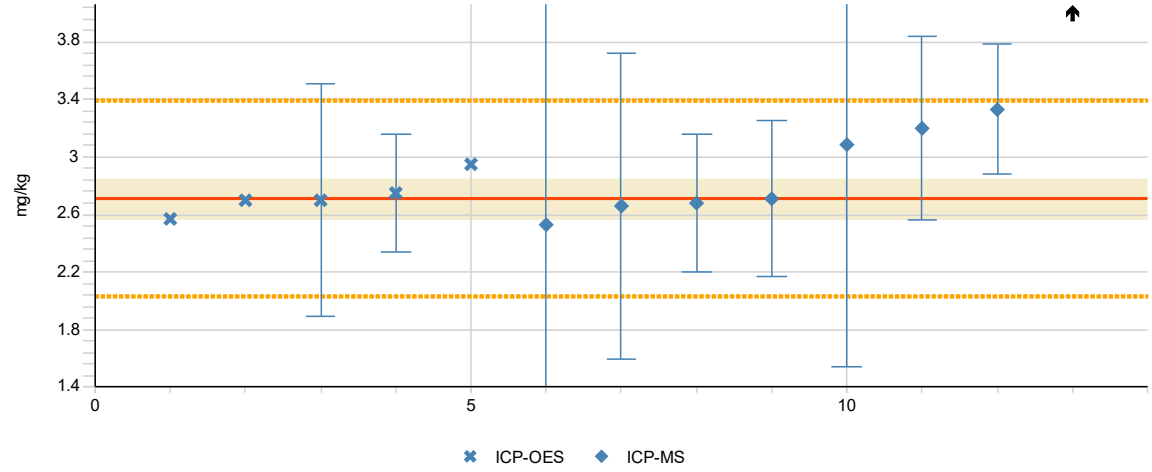
Measurand Conductivity 25 Sample RT1LS_8



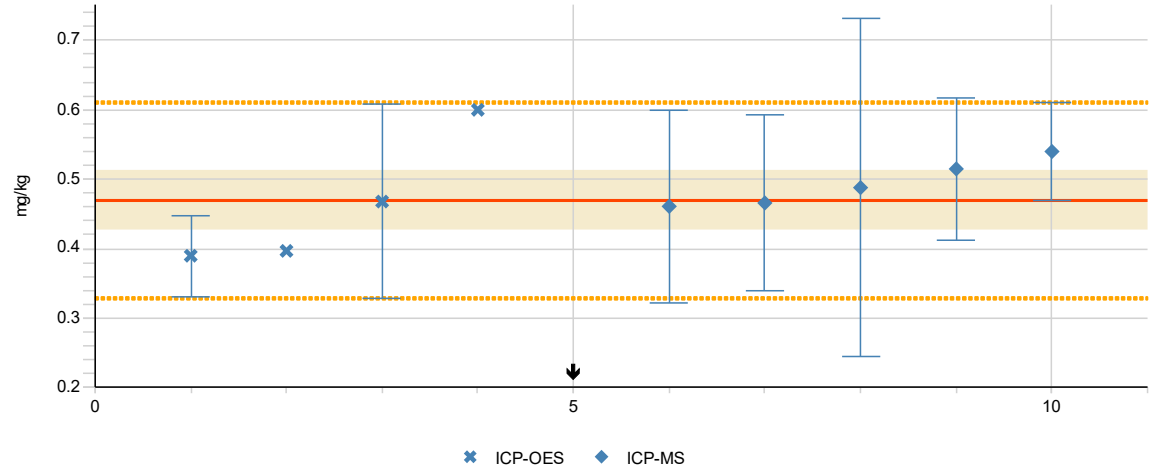
Measurand Cr Sample RT1LS_2



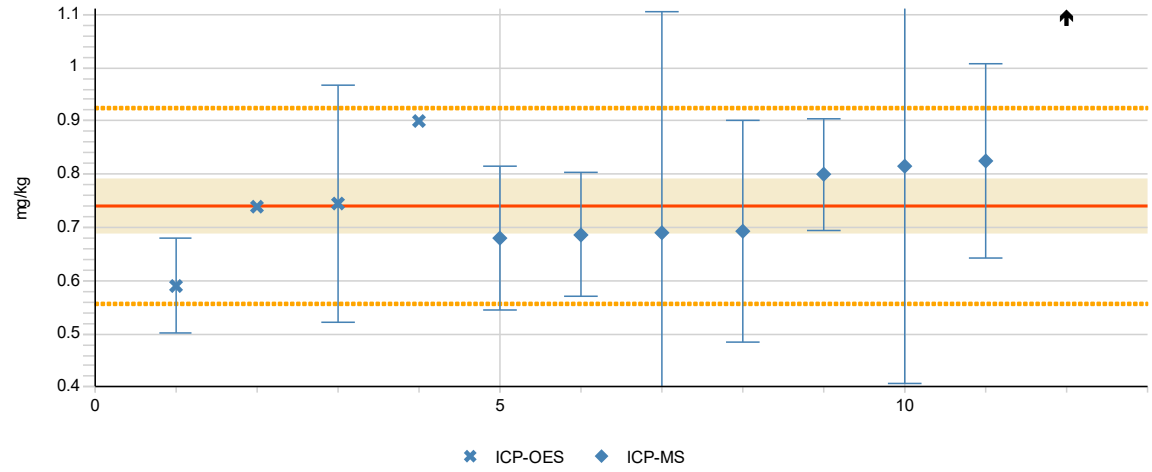
Measurand Cr Sample RT1LS10



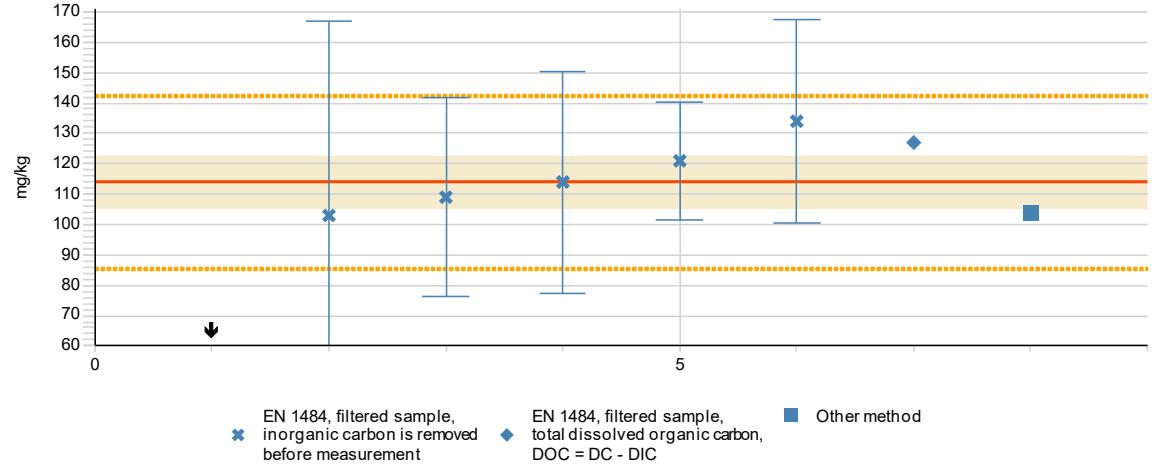
Measurand Cu Sample RT1LS_2



Measurand Cu Sample RT1LS10



Measurand DOC Sample RT1LS_2



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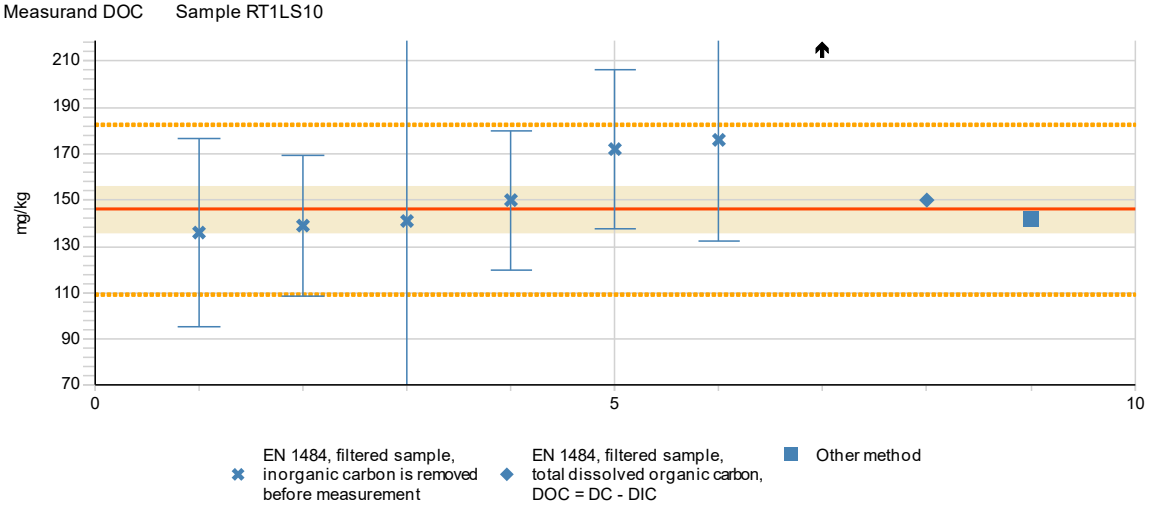

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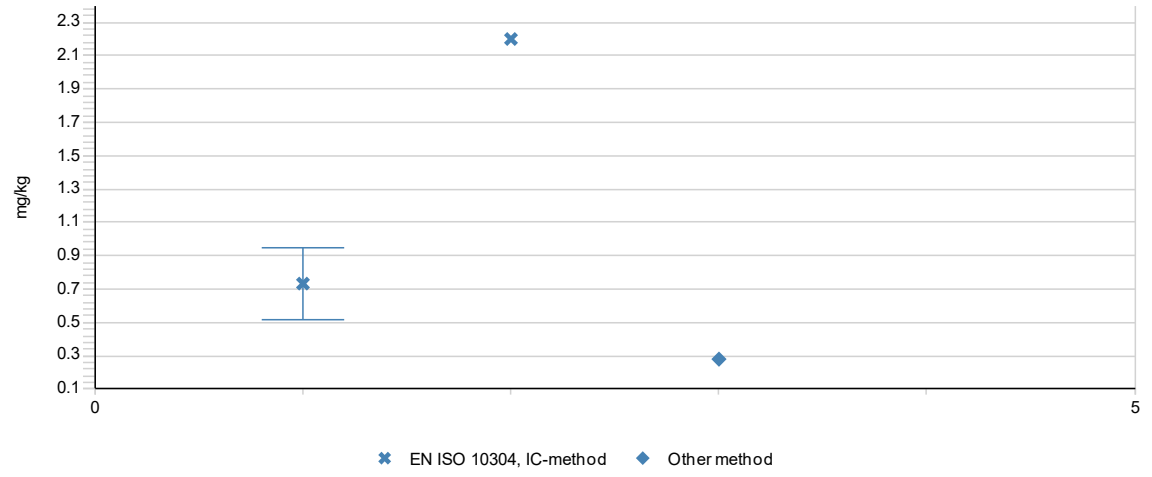

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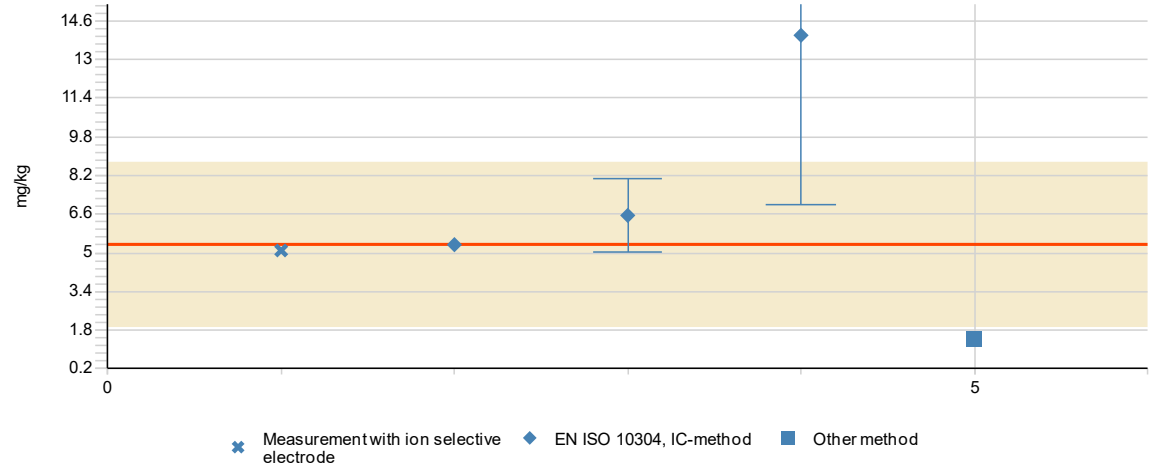
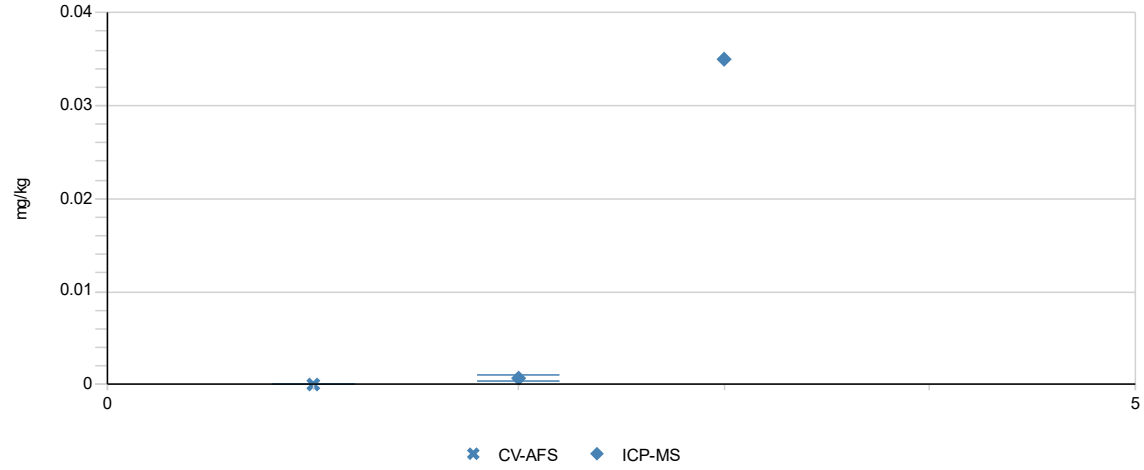
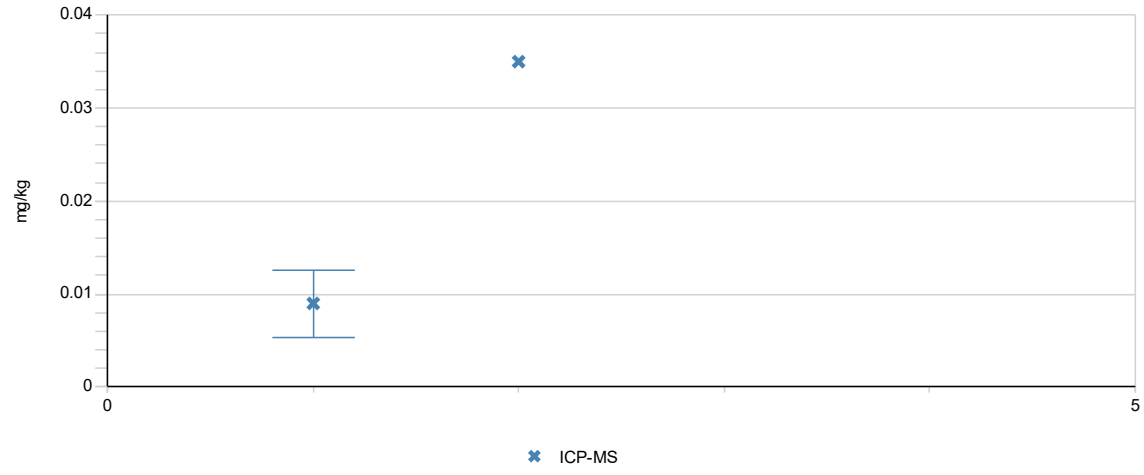


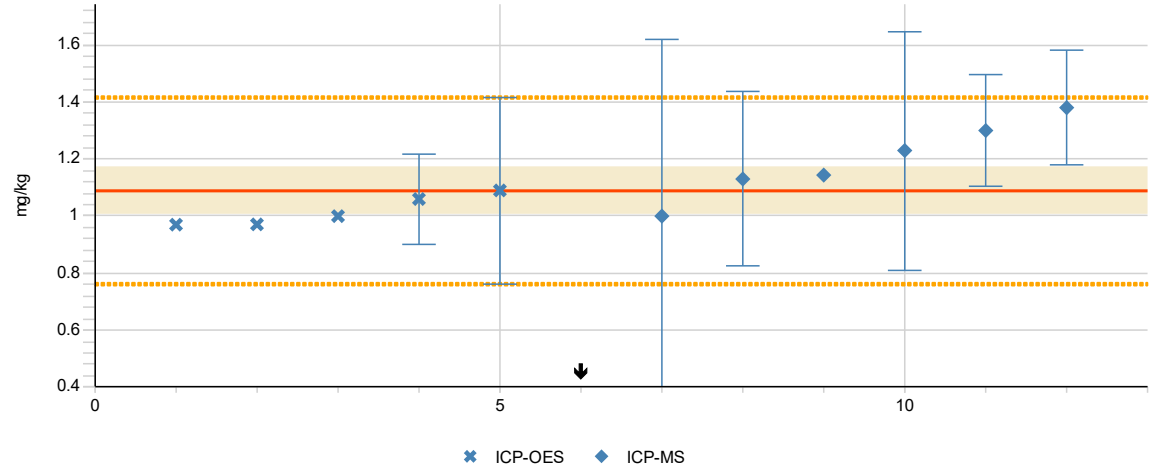
Measurand Hg Sample RT1LS_2



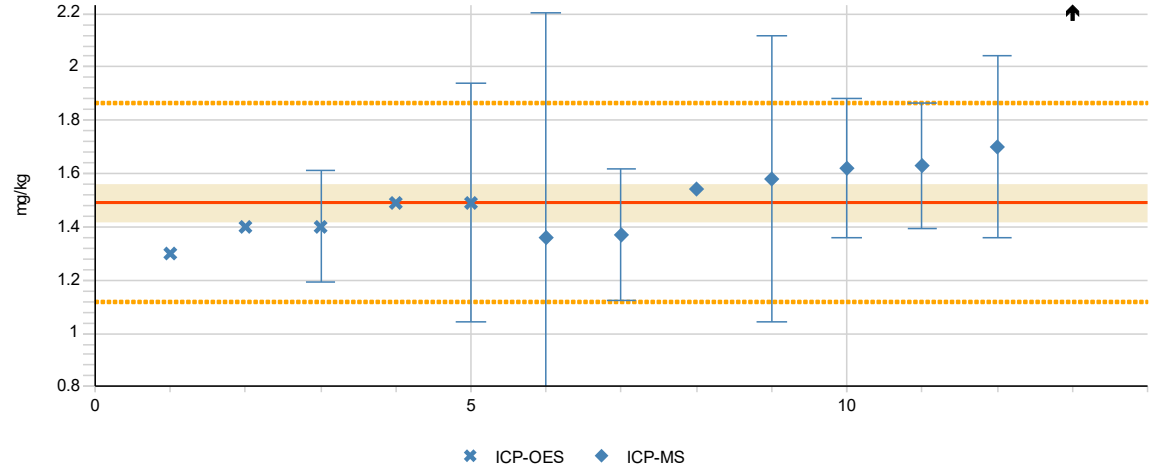
Measurand Hg Sample RT1LS10



Measurand Mo Sample RT1LS_2



Measurand Mo Sample RT1LS10



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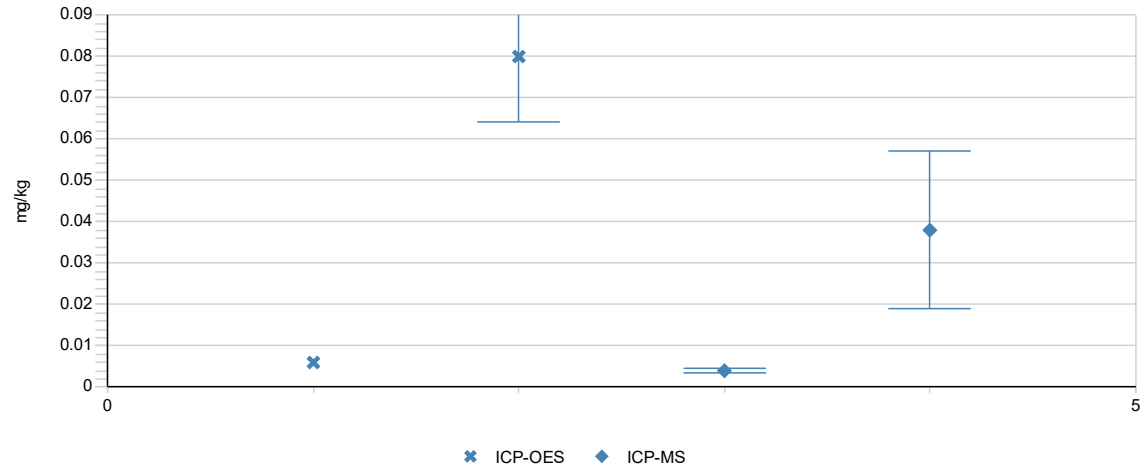

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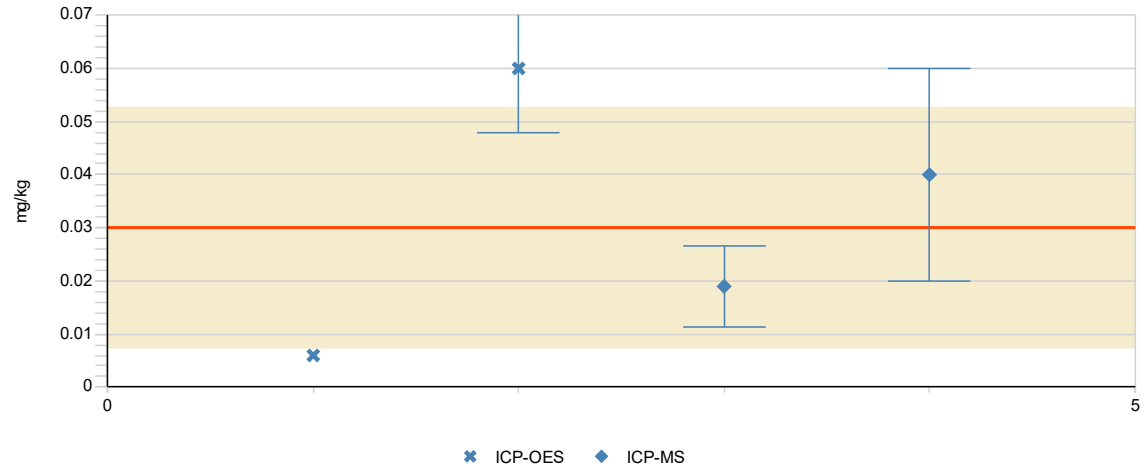
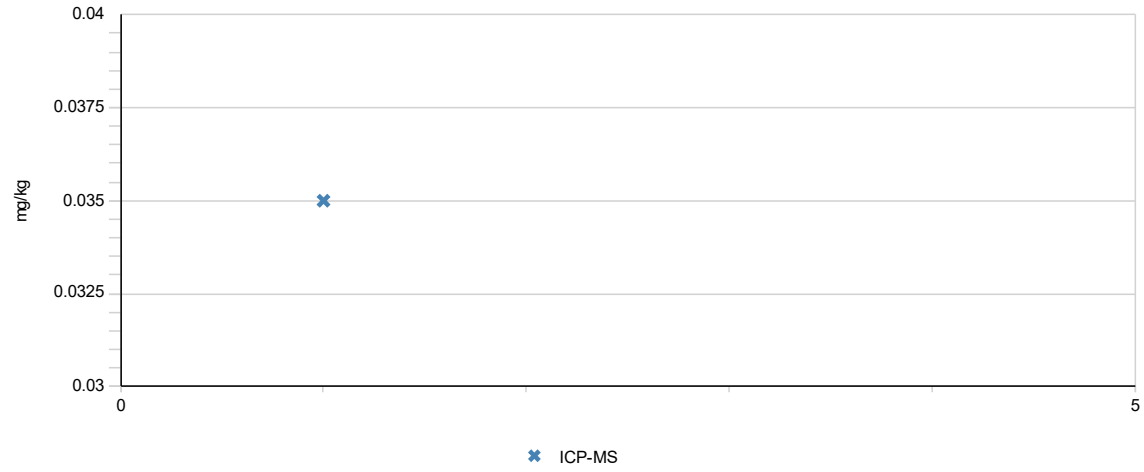


Measurand Pb Sample RT1LS_2



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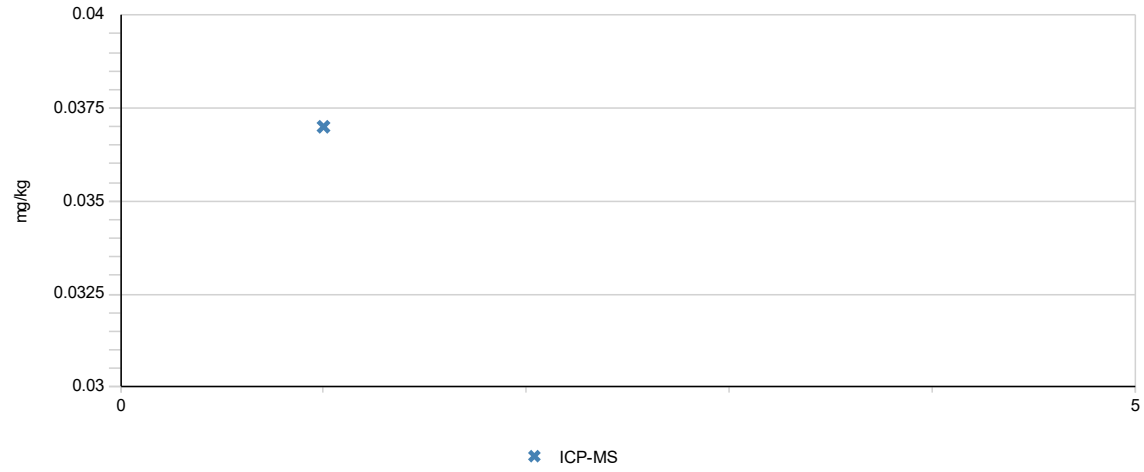
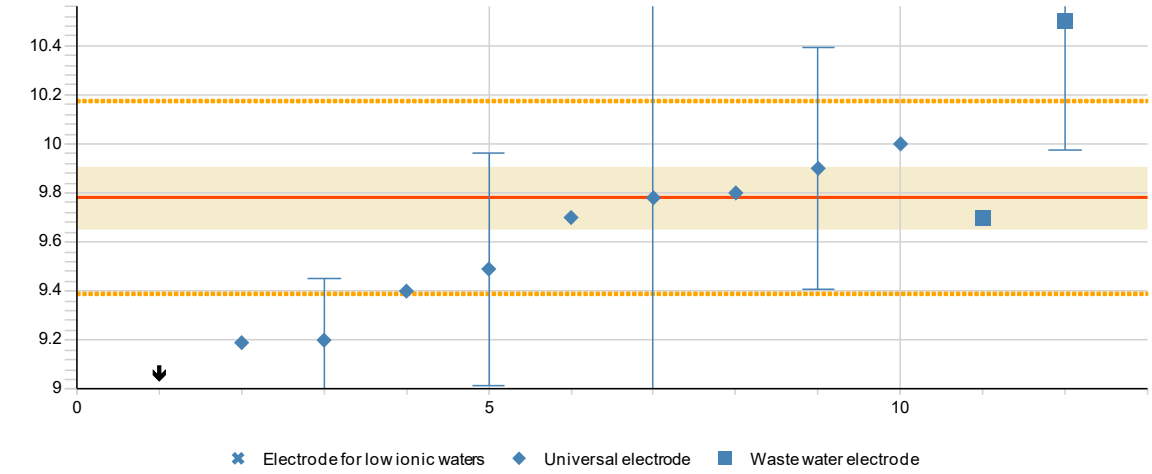
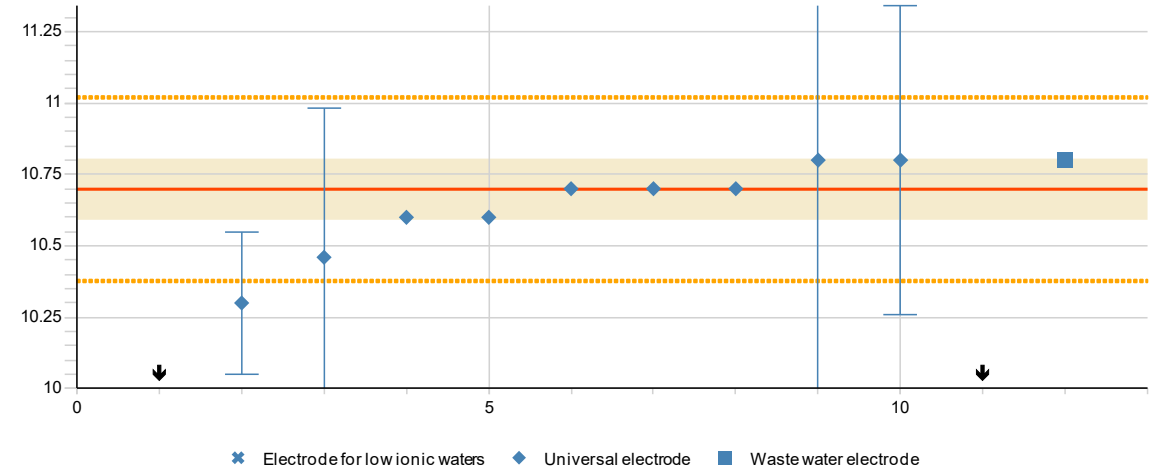


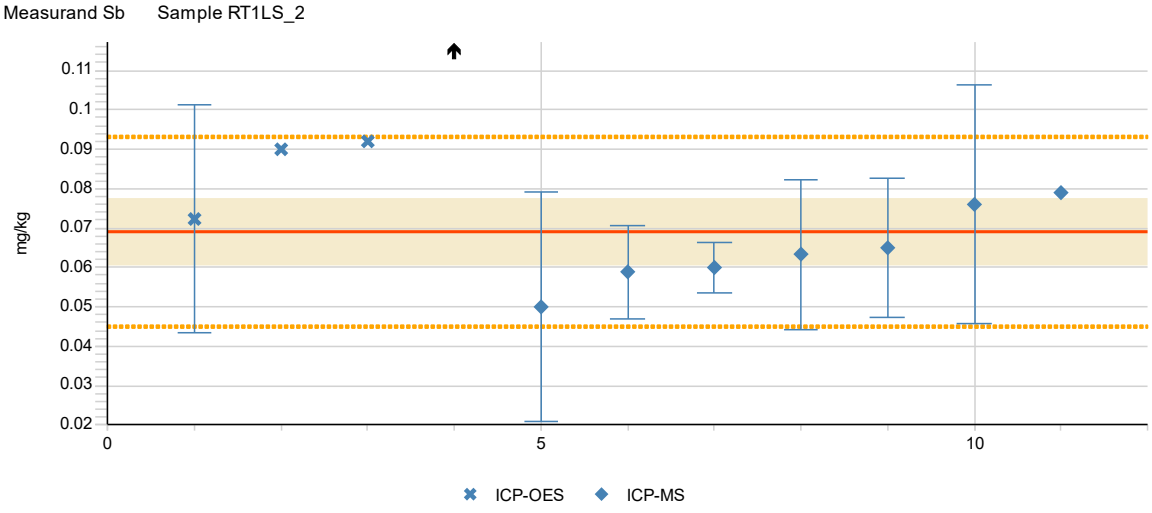
Measurand pH Sample RT1LS_2



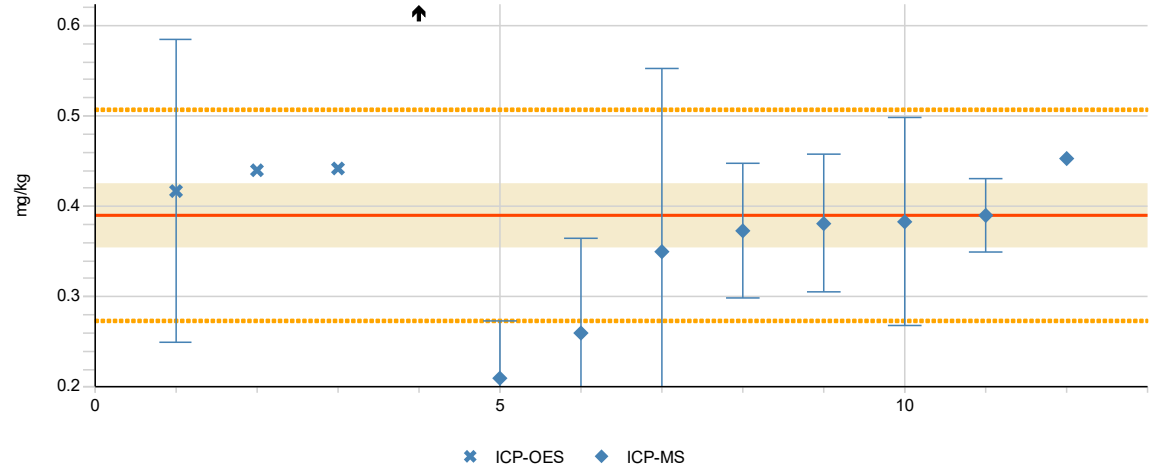
Measurand pH Sample RT1LS_8



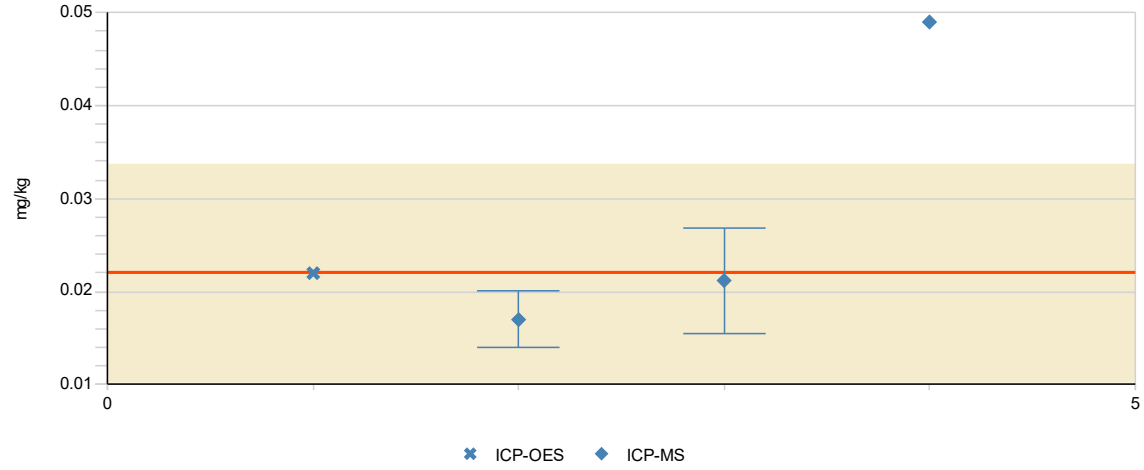
Measurand Sb Sample RT1LS_2



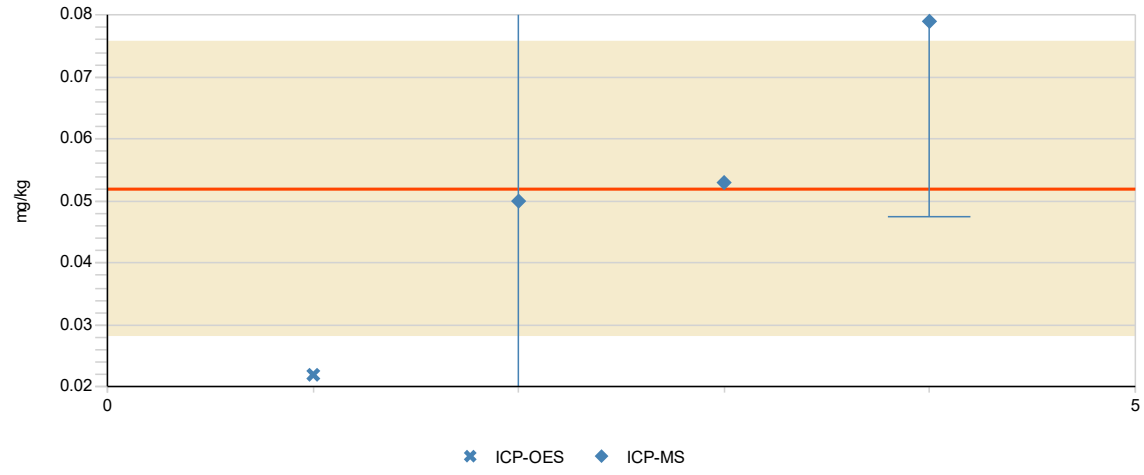
Measurand Sb Sample RT1LS10



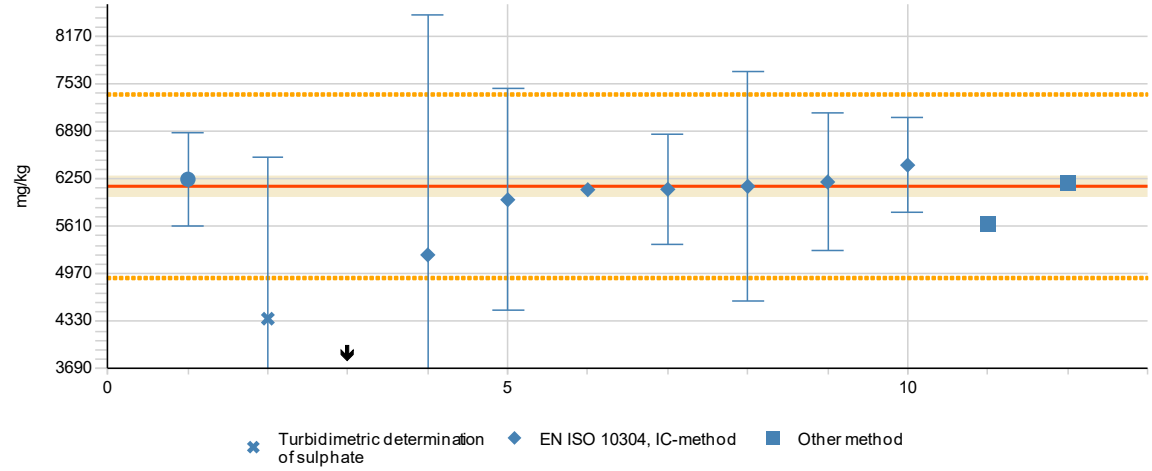
Measurand Se Sample RT1LS_2



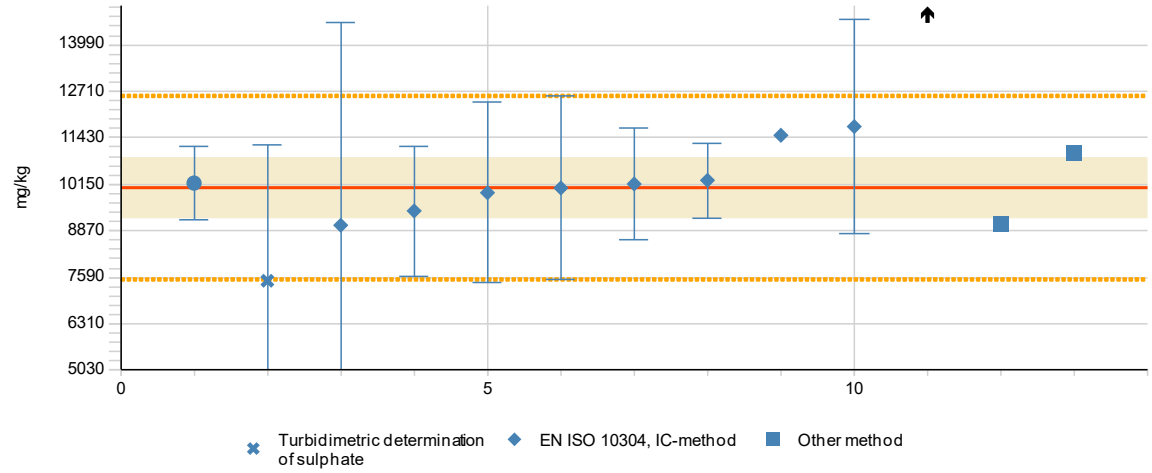
Measurand Se Sample RT1LS10



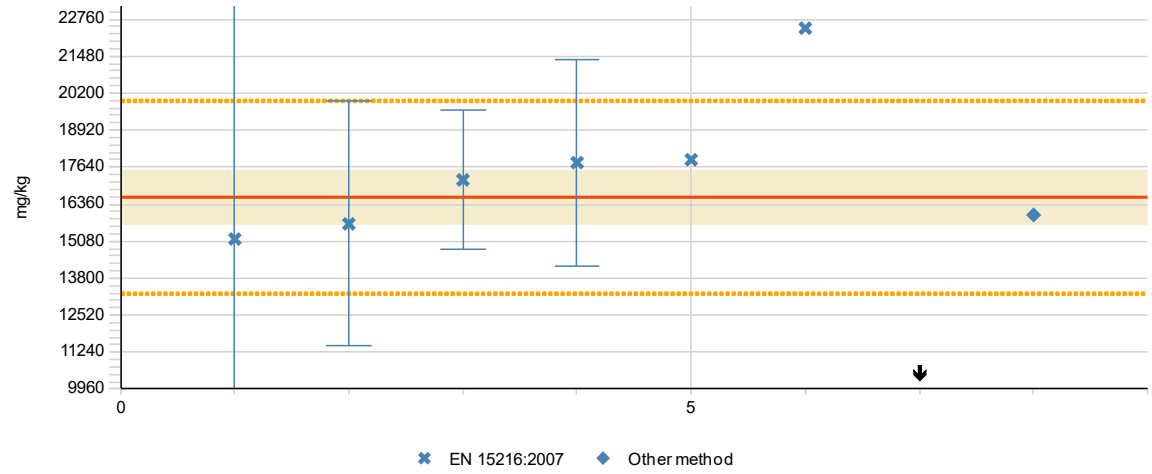
Measurand SO_4 Sample RT1LS_2



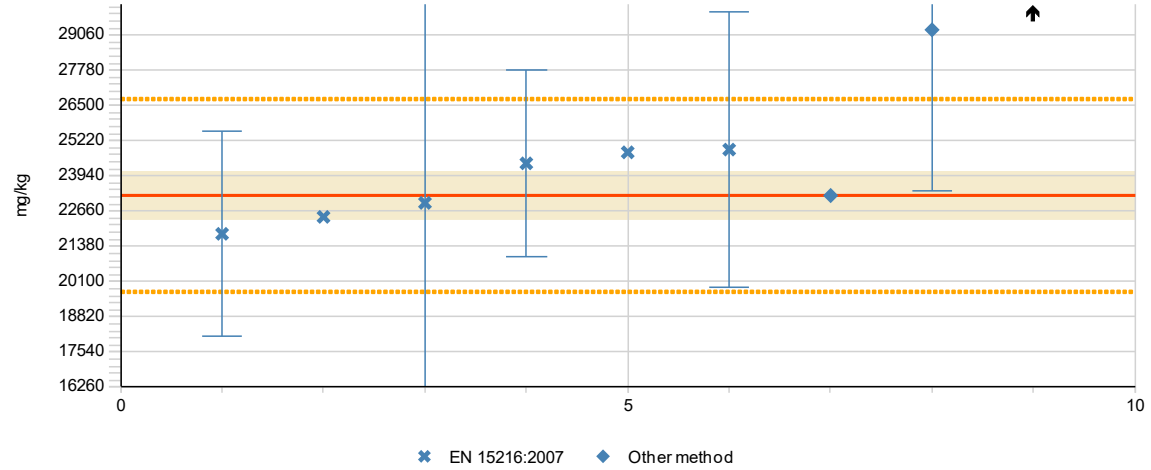
Measurand SO_4 Sample RT1LS10



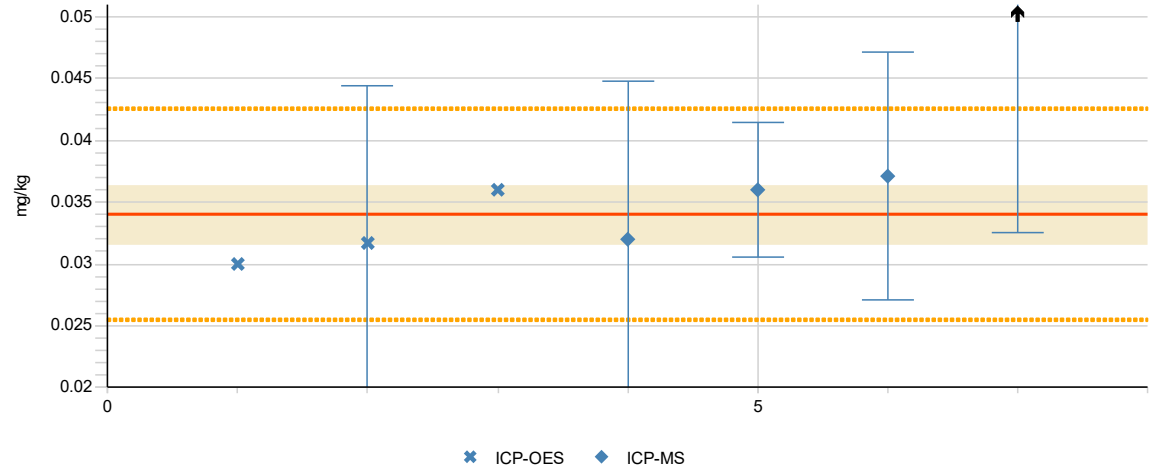
Measurand TDS Sample RT1LS_2



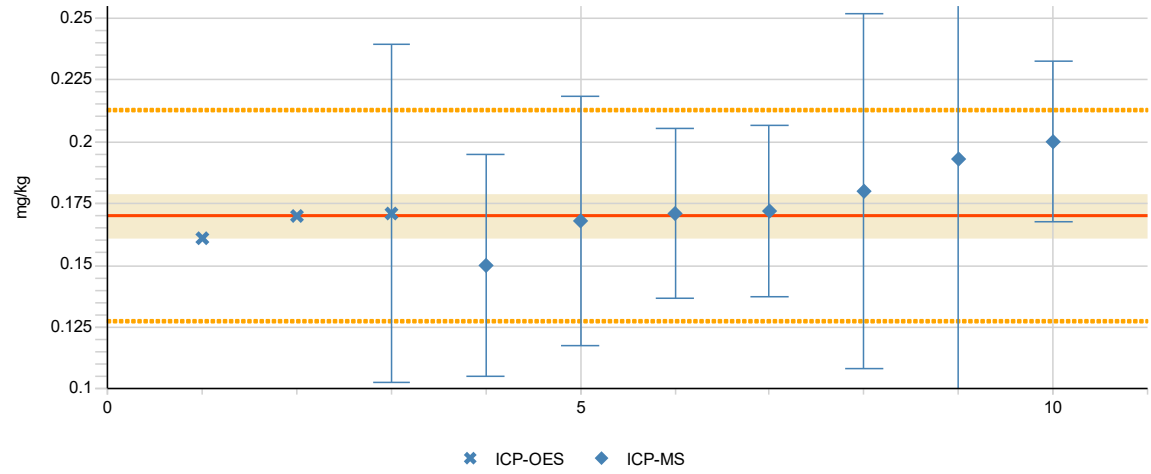
Measurand TDS Sample RT1LS10

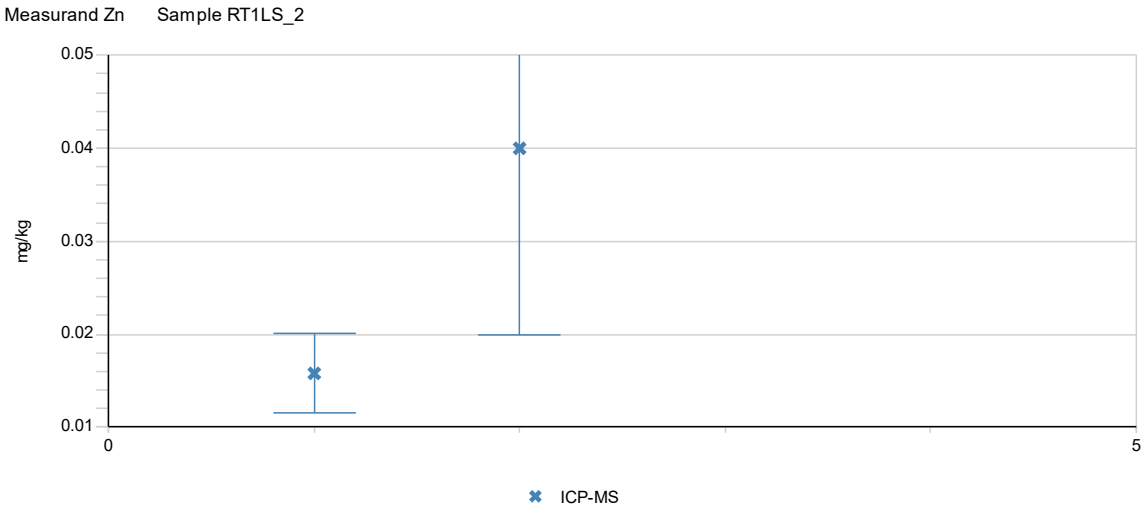


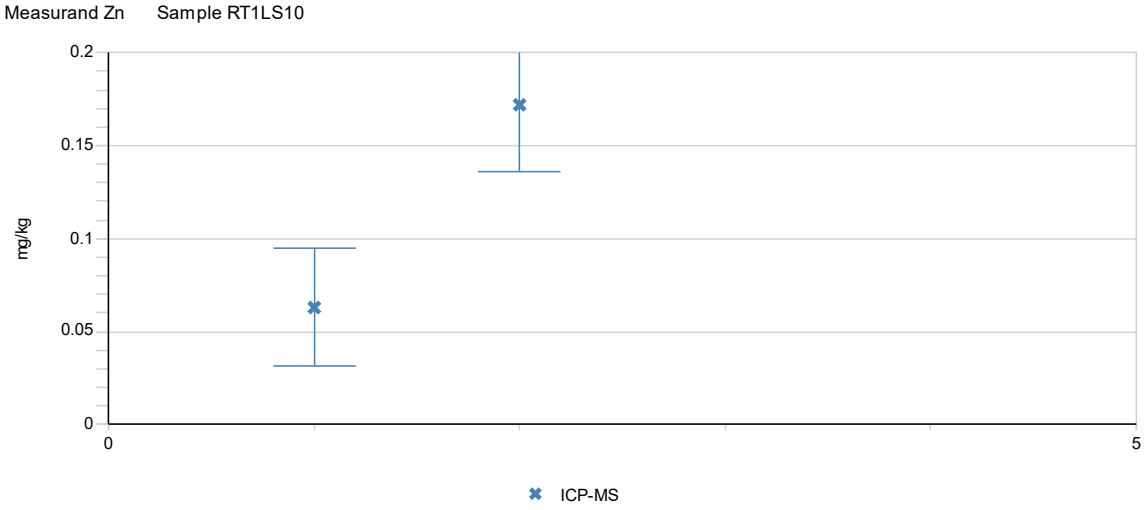
Measurand V Sample RT1LS_2



Measurand V Sample RT1LS10

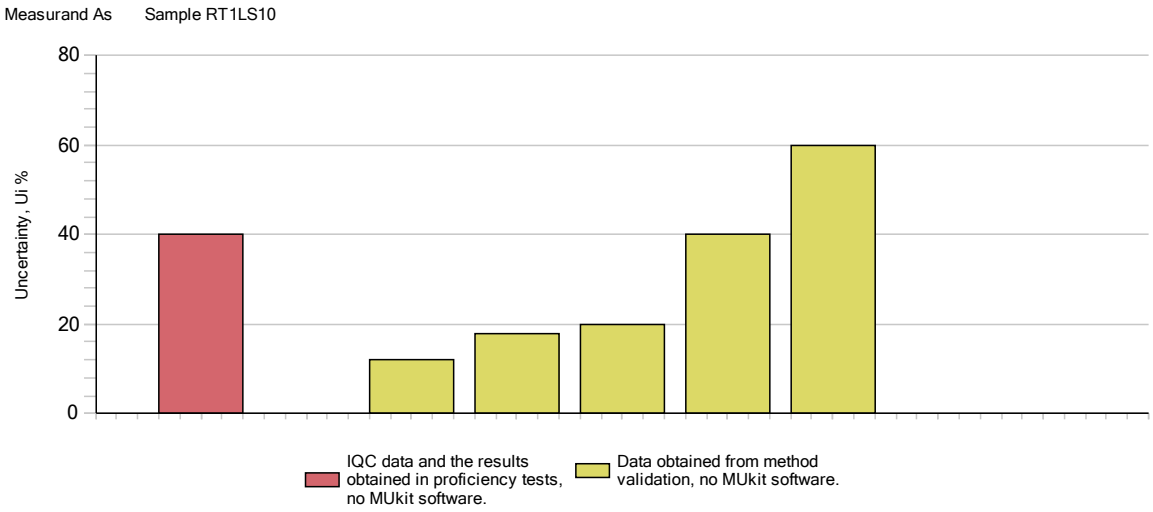


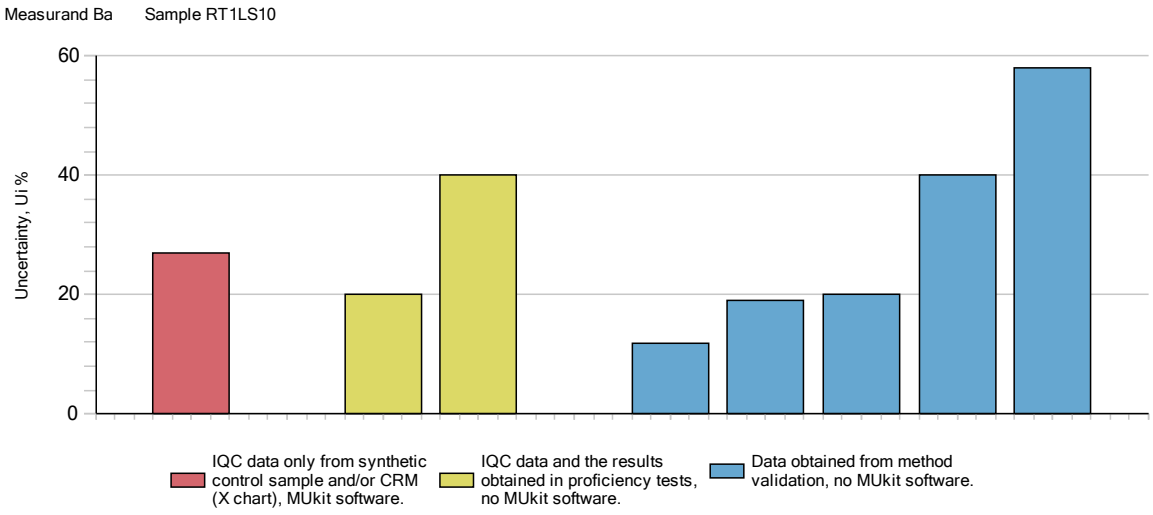

Measurand Zn Sample RT1LS_2
0.05
0.04
0.03
0.02
0.01
mg/kg
0
5
ICP-MS


Measurand Zn Sample RT1LS10
0.2
0.15
0.1
0.05
0
mg/kg
0
5
ICP-MS

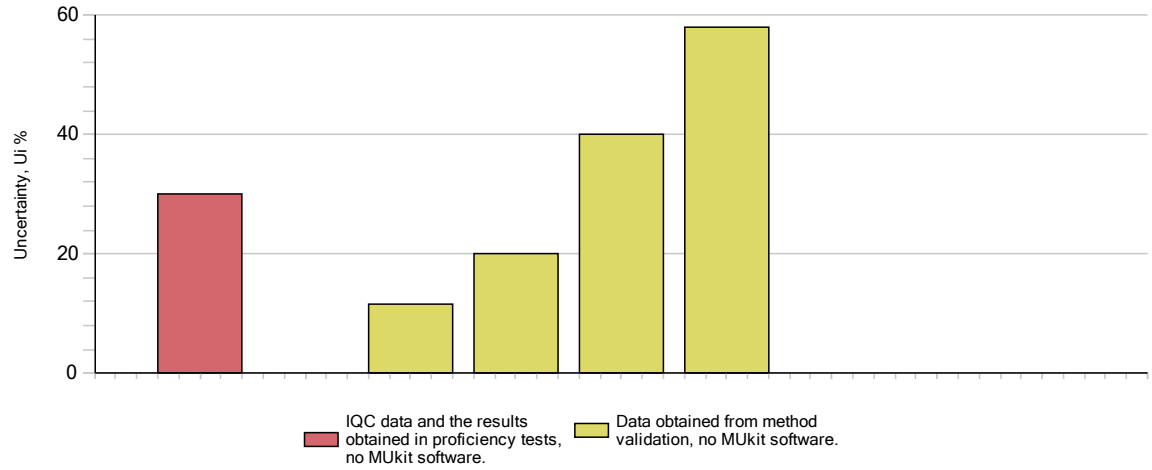
APPENDIX 14: Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using IQC data or data from method validation [9, 10].

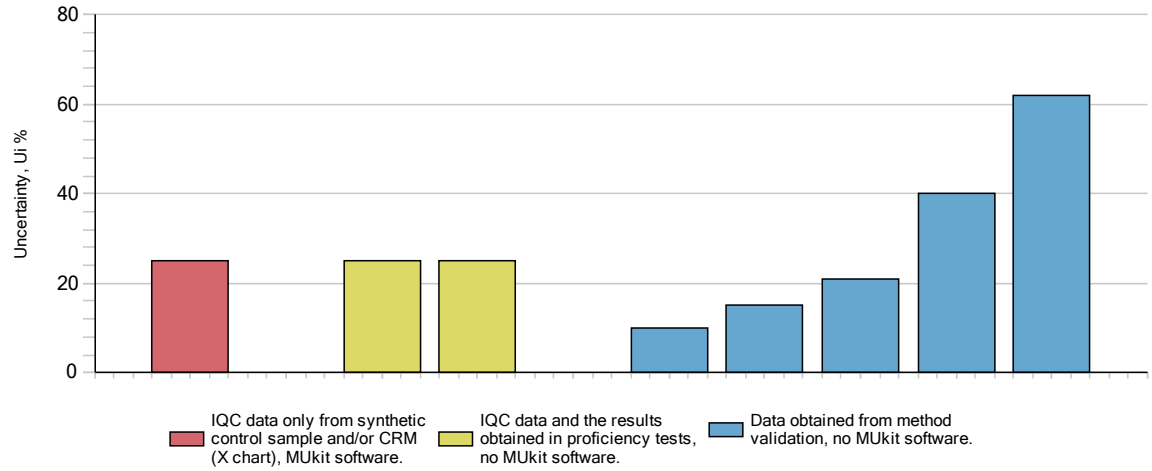




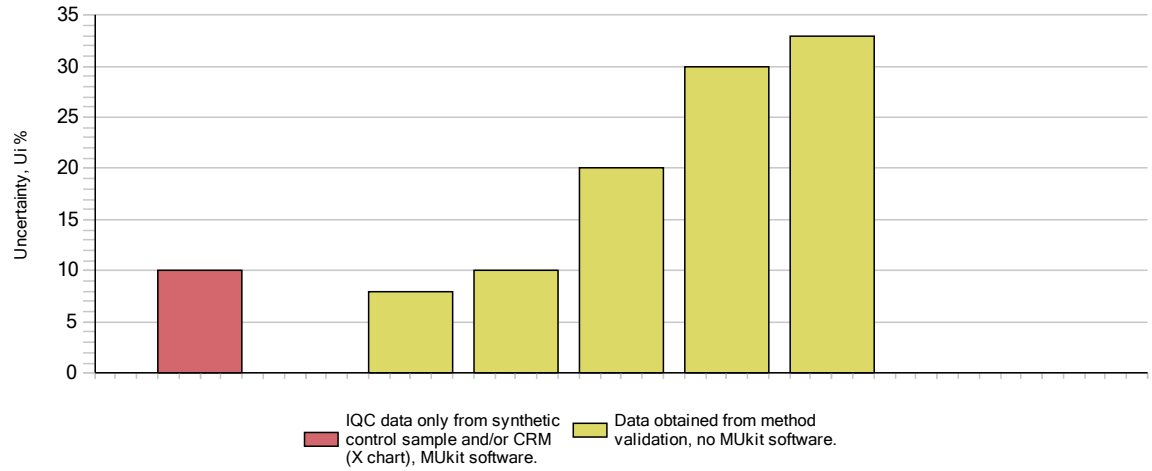
Measurand Cd Sample RT1LS10



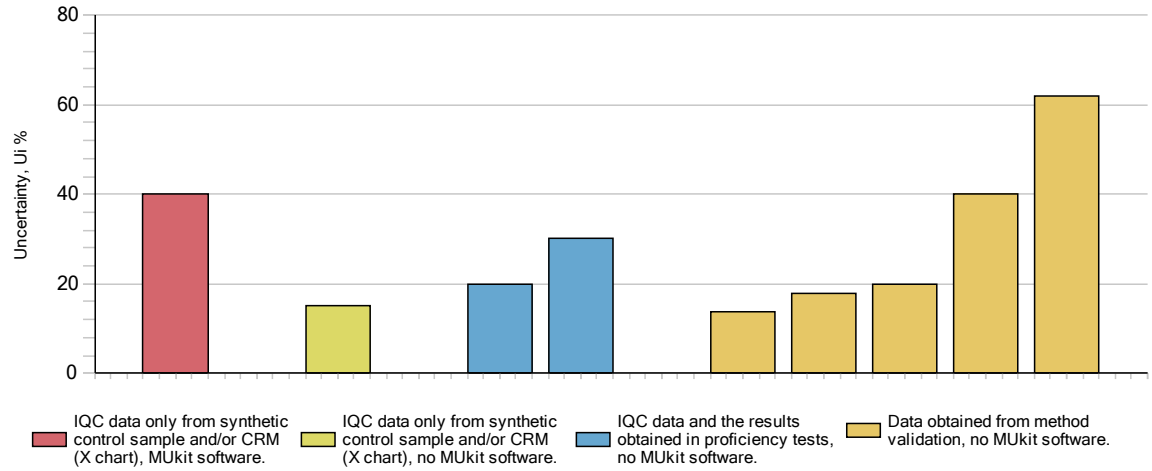
Measurand Cl Sample RT1LS10



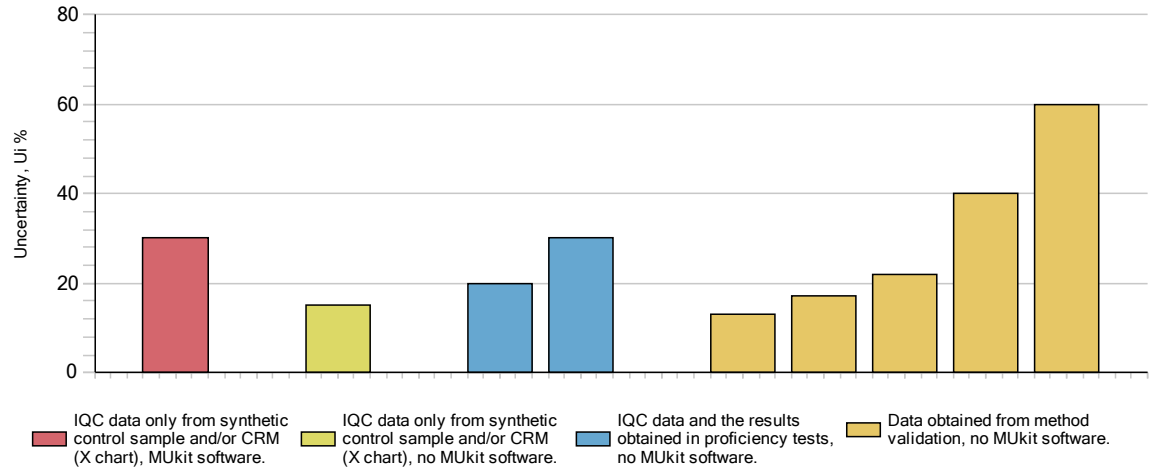
Measurand Conductivity 25 Sample RT1LS_2



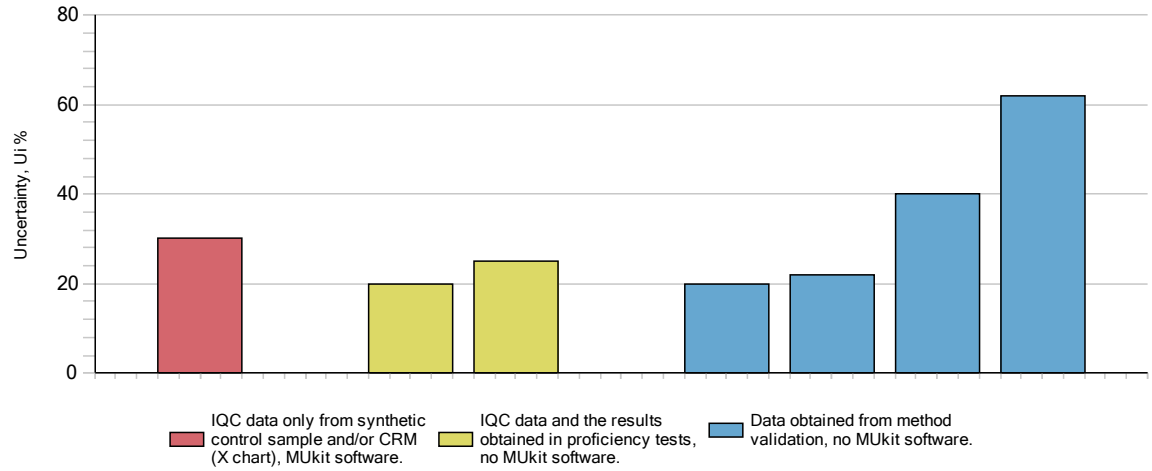
Measurand Cr Sample RT1LS10



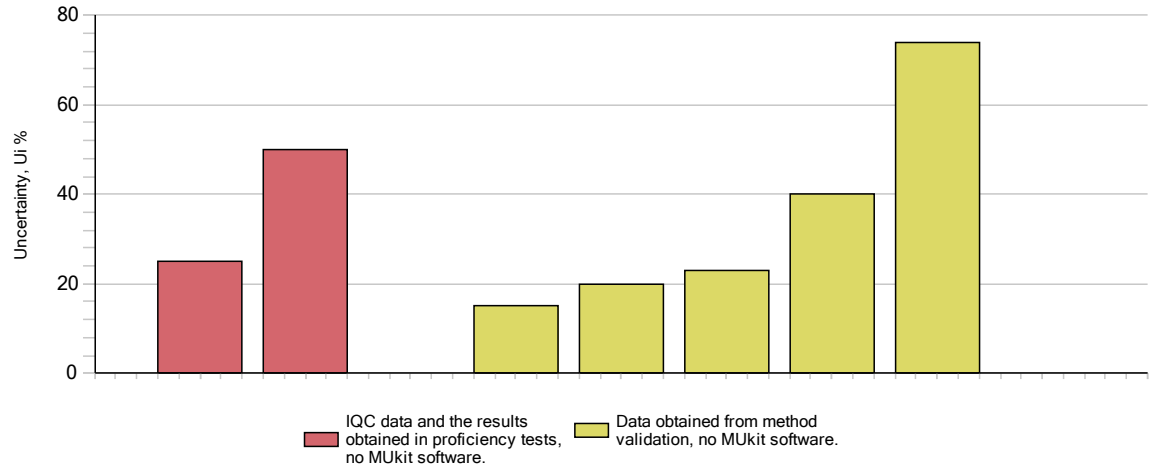
Measurand Cu Sample RT1LS10



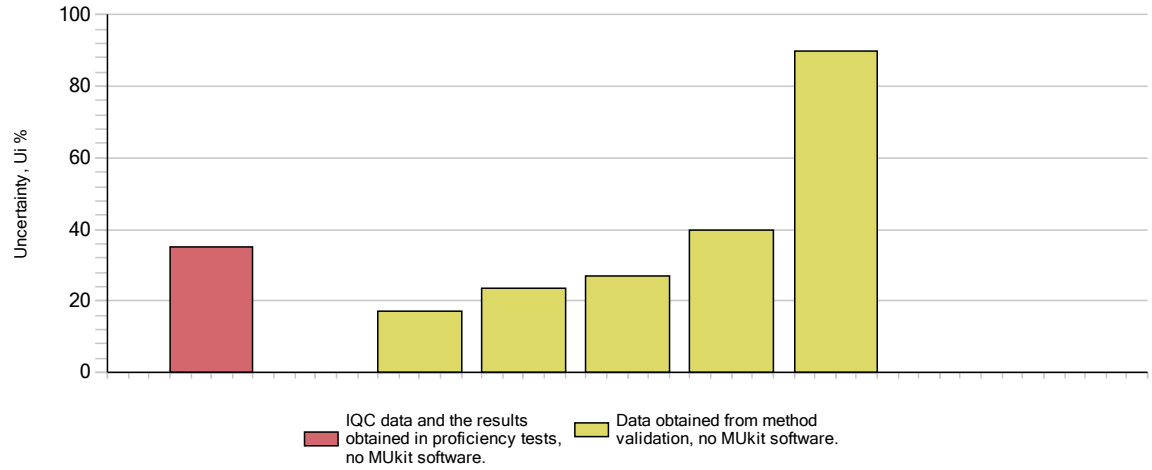
Measurand DOC Sample RT1LS10



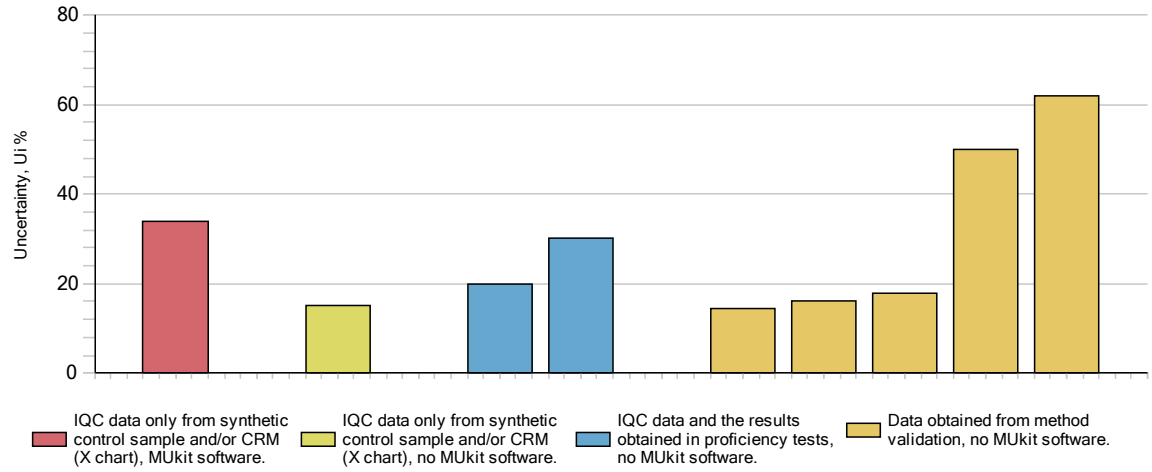
Measurand F Sample RT1LS10



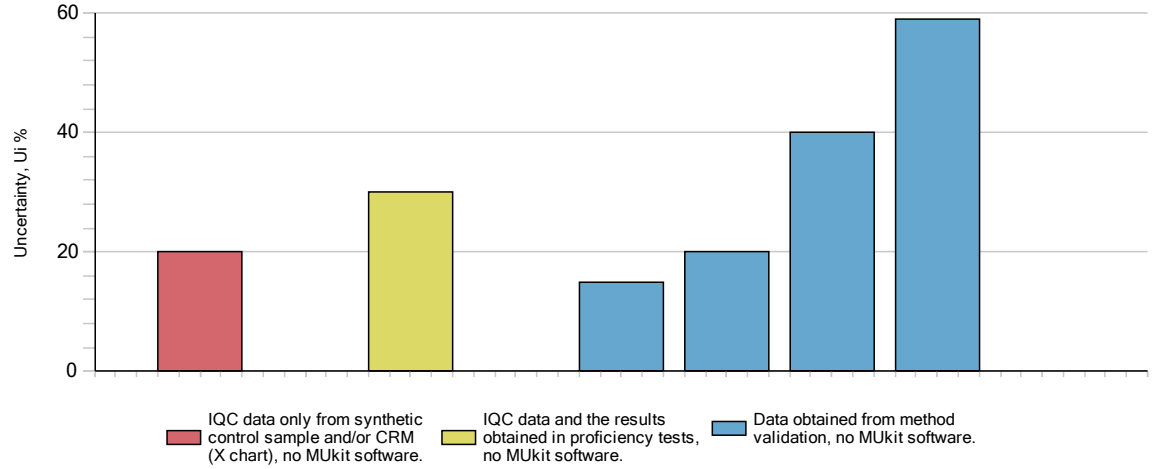
Measurand Hg Sample RT1LS_2



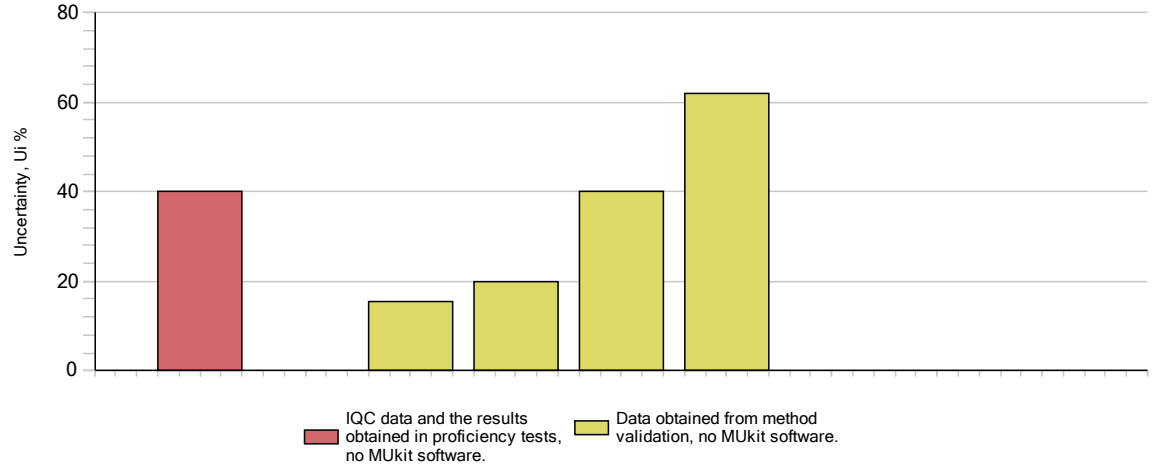
Measurand Mo Sample RT1LS10



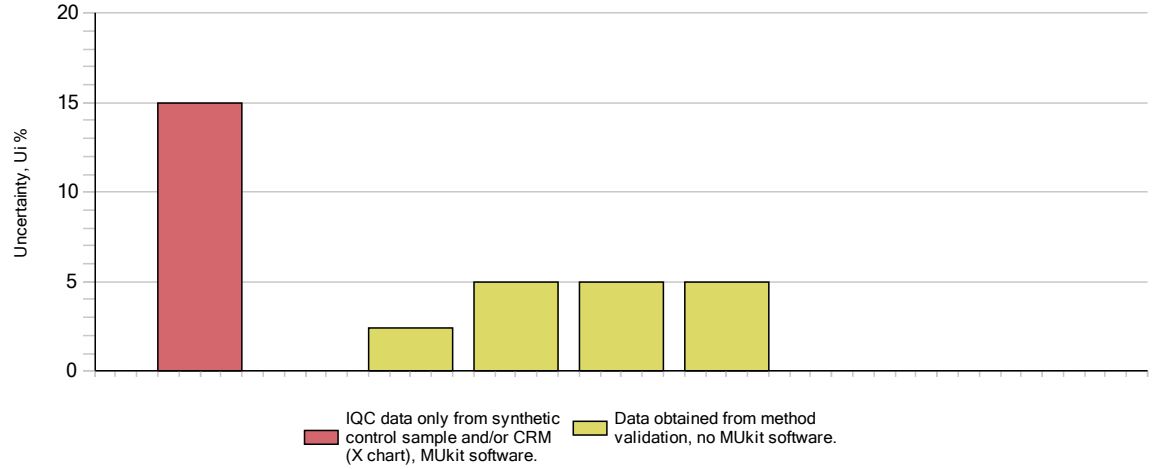
Measurand Ni Sample RT1LS10



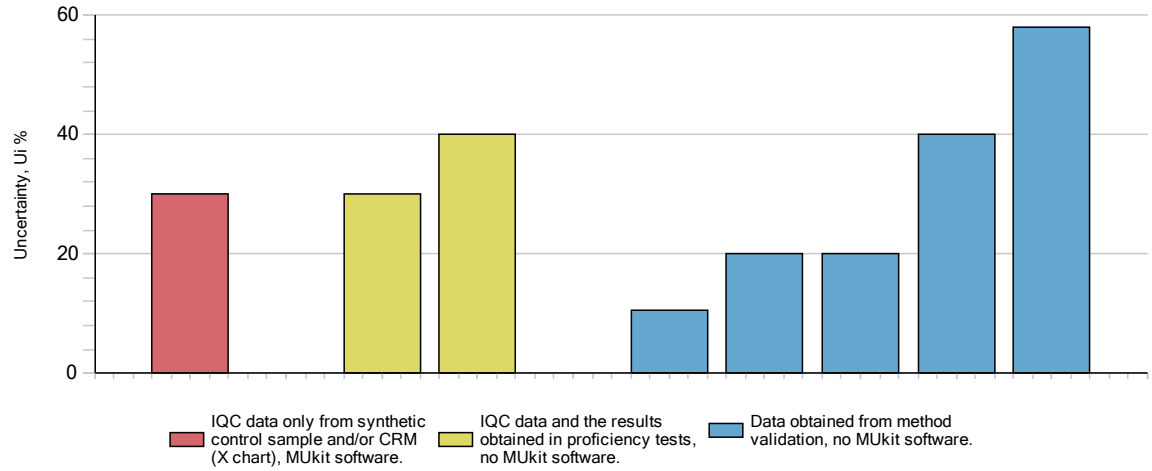
Measurand Pb Sample RT1LS_2



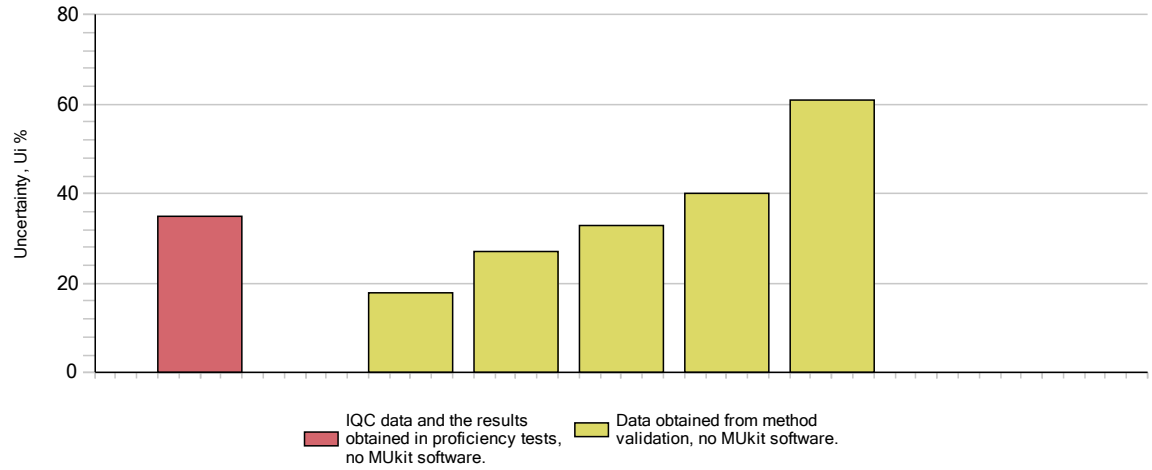
Measurand pH Sample RT1LS_8



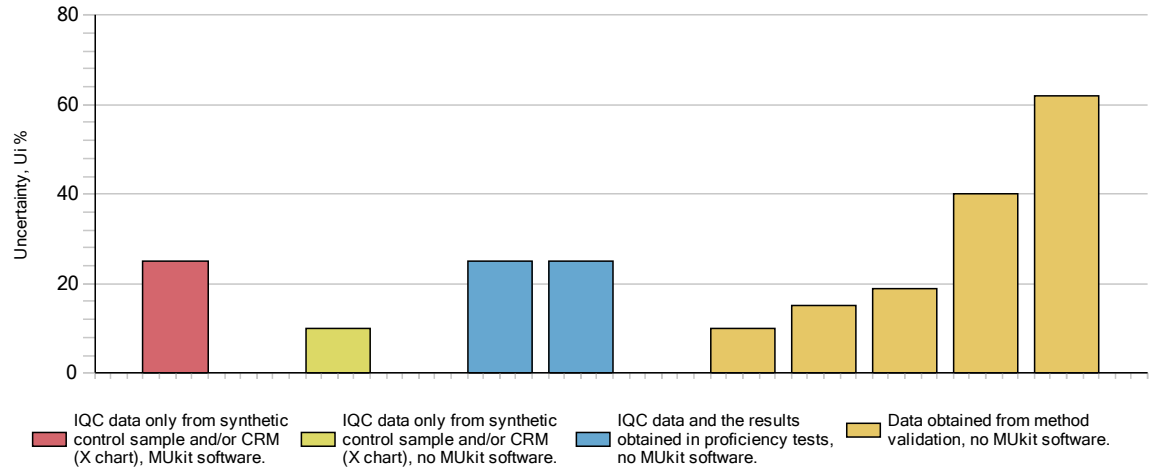
Measurand Sb Sample RT1LS10



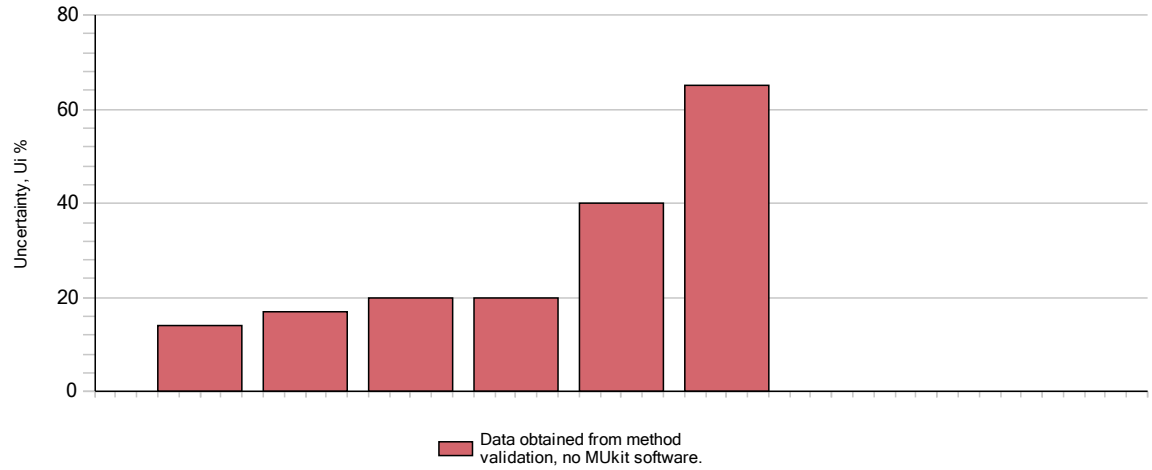
Measurand Se Sample RT1LS_2



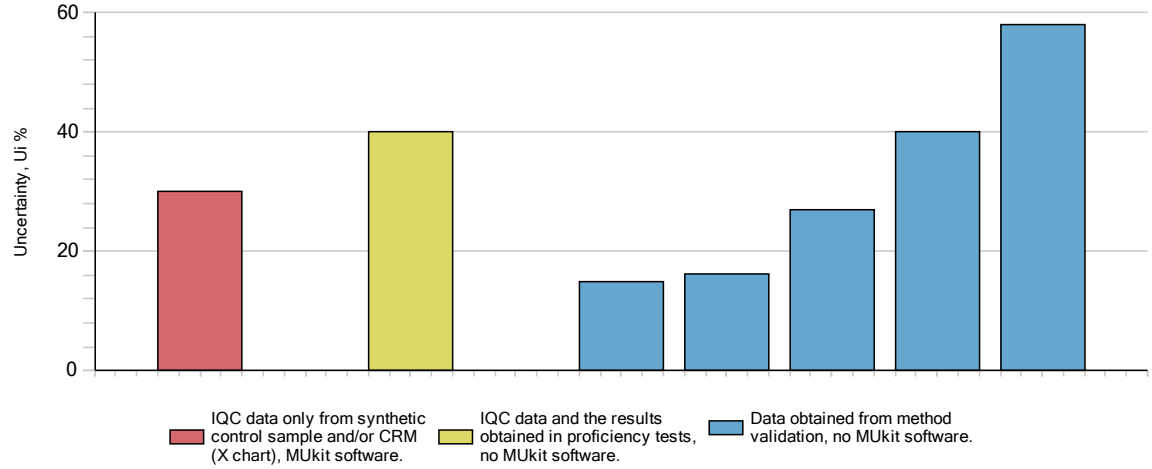
Measurand SO_4 Sample RT1LS10



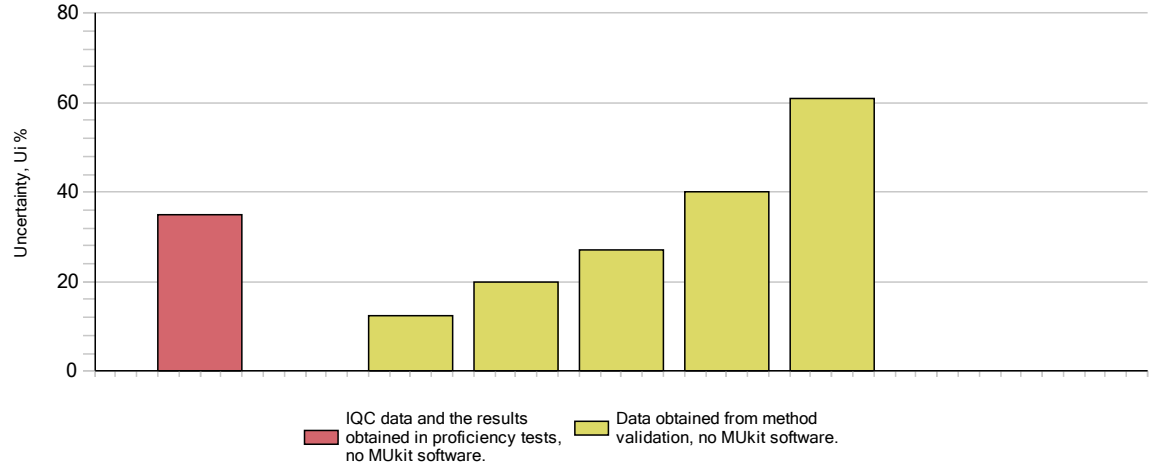
Measurand TDS Sample RT1LS10



Measurand V Sample RT1LS_2



Measurand Zn Sample RT1LS_2



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